

*Handwritten:*

# A Textbook of Physical Chemistry

Volume 4  
(SI Units)

Quantum Chemistry and Molecular Spectroscopy

Fourth Edition

K L KAPOOR

## A Textbook of Physical Chemistry

- Volume I : States of Matter and Ions in Solution
- Volume II : Thermodynamics and Chemical Equilibrium
- Volume III : Applications of Thermodynamics
- Volume IV : Quantum Chemistry and Molecular Spectroscopy
- Volume V : Dynamics of Chemical Reactions, Statistical Thermodynamics, and Macromolecules
- Volume VI : Computational Aspects in Physical Chemistry

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To  
My Mother  
and  
to the  
Memory of My Father

## Preface to the Fourth Edition

The first edition of the fourth volume of the *Textbook of Physical Chemistry* was bifurcated into two volumes in 2004. Volume 4 included chapters on atomic structure, chemical bonding, electrical and magnetic properties, and molecular spectroscopy, while Volume 5 included adsorption, chemical kinetics, photochemistry, statistical thermodynamics and macromolecules.

Without disturbing the main format of chapters, the revised edition of Volume 4 includes the following features:

- The book incorporates the IUPAC recommendations in the field of Physical Chemistry.
- The entire subject matter has been presented with the proper subheadings to facilitate the reader to understand the text in a more systematic manner.
- SI units are used throughout.
- In the second edition, supplementary materials in the form of annexures were added in the chapter Wave Mechanics, Energy Quantization and Atomic Structure. These include solution of Schrödinger equation for a harmonic oscillator using the power series method, operators for the components of angular momentum, transformation of Laplacian operator from Cartesian coordinates to spherical polar coordinates, splitting of Schrödinger equation of hydrogen atom, commutators of angular momentum operators and atomic units. Besides these, a brief description of atomic and molecular term symbols and the derivation of selection rule for a harmonic oscillator were also included.
- This new edition of Volume 4 includes a new Chapter entitled 'Molecular Symmetry and Its Applications'. Besides this, additional supplementary materials as annexures have been added. These include details of perturbation theory and variational method, proof of variational theorem, evaluation of  $J$ ,  $K$  and  $S$  integrals in the LCAO-MO treatment of  $H_2^+$ , the factorization method for evaluating eigenvalues of harmonic oscillator and angular momentum, electronic transitions in hydrogen atom including spin-orbit coupling, and derivation of expression of orientation polarizability.

Volume 4 describes atomic structure and molecular spectroscopy in five chapters, viz., Wave Mechanics, Energy Quantization and Atomic Structure, Theories of Covalent Bond; Electrical and Magnetic Properties; Molecular Spectroscopy and Molecular Symmetry and Its Applications.

Lastly, I wish to extend my appreciation to the students and teachers of Delhi University for the constructive suggestions in bringing out this edition of the book. I also record my thanks to my family members Pratima, Saurabh and Urvasi, and Surabhi and Jugnu for their appreciation and constant encouragement.

K L Kapoor

## Preface to the First Edition

In recent years the teaching curriculum of physical chemistry in many Indian universities has been restructured with a greater emphasis on a theoretical and conceptual methodology and the applications of the underlying basic concepts and principles. This shift in the emphasis, as I have observed, has unduly frightened the undergraduates whose performance in physical chemistry has been otherwise generally far from satisfactory. This poor performance is partly because of the nonavailability of a comprehensive textbook which also lays adequate stress on the logical deduction and solution of numericals and related problems. Naturally, the students find themselves unduly constrained when they are forced to refer to various books to collect the necessary reading material. It is primarily to help these students that I have ventured to present a textbook which provides a systematic and comprehensive coverage of the theory as well as of the illustration of the applications thereof.

The present book grew out of more than a decade of classroom teaching through lecture-notes and assignments prepared for my students of B.Sc. (General) and B.Sc. (Hons). The systematic structure of the book is assigned to cover the major topics of physical chemistry in four different volumes. Volume I discusses the states of matter and ions in solutions. It comprises five chapters on the gaseous state, physical properties of liquids, solid state, ionic equilibria and conductance. Volume II describes the basic principles of thermodynamics and chemical equilibrium in seven chapters, viz., introduction and mathematical background, zeroth and first laws of thermodynamics, thermochemistry, second law of thermodynamics, criteria for equilibrium and  $A$  and  $G$  functions, systems of variable composition, and thermodynamics of chemical reactions. Volume III seeks to present the applications of thermodynamics to the equilibria between phases, colligative properties, phase rule, solutions, phase diagrams of one-, two- and three component systems, and electrochemical cells. Volume IV deals with quantum chemistry and the dynamics of chemical reactions: it focuses on atomic structure, chemical bonding, electrical and magnetic properties, molecular spectroscopy, adsorption, chemical kinetics, catalysis and photochemistry.

The study of physical chemistry is incomplete if the student confines himself to the ambit of theoretical discussion of the subject. He must grasp the practical significance of the basic theory in all its ramifications and develop a clear perspective to appreciate various problems and how they can be solved. It is here that this book merits mention. Apart from having a lucid style and simplicity of expression, the book has a wealth of carefully selected examples and solved illustrations. Further, three types of problems with different objectives in view are listed at the end of each chapter: (1) Revisionary Problems, (2) Try Yourself Problems, and (3) Numerical



Problems. Under Revisionary Problems, only those problems pertaining to the text are included which should afford an opportunity to the students in self-evaluation. In Try Yourself Problems, the problems related to the text but not highlighted therein are provided. Such problems will help the students extend their knowledge of the chapter to closely related problems. Finally, unsolved numericals are pieced together for the practice of the students.

Though the present textbook is written on the basis of the syllabi prescribed for undergraduate courses of the University of Delhi, it will also prove useful to students of other universities, since the content of physical chemistry remains the same everywhere. In general, the SI units (*System International d' unite's*) along with some of the common non-SI units such as atm, mmHg, etc., have been used in the book.

I wish to acknowledge my greatest indebtedness to my teacher, Prof. R. P. Mitra, who instilled in me the spirit of scientific inquiry. I also record my sense of appreciation to my students and colleagues at Hindu College, University of Delhi, for their comments, constructive criticism and valuable suggestions towards improvement of the book. I would also like to thank Dr M. Katyal for his valuable suggestions and keen interest in the publication of the book. The subsidy from the National Book Trust, India, is duly acknowledged. I thank Mr Purn Singh for typing the manuscript. Finally, my special thanks go to my wife Pratima for her encouragement, patience and understanding.

The author takes the entire responsibility for any error or ambiguity in fact or opinion that may have found its way into this book. Comments and criticism from readers will therefore be highly appreciated and incorporated in subsequent editions.

New Delhi  
March, 1985

**K L Kapoor**

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# 1 Wave Mechanics, Energy Quantization and Atomic Structure

## 1.1 TOWARDS QUANTUM THEORY

### Introduction

During the latter of the nineteenth century, a number of experimental observations were reported which could not be explained on the basis of the classical theory. Among these were the spectral distribution of energy in black-body radiation, photoelectric effect, variation of heat capacity of monatomic solids with temperature, and the discrete spectra emitted by excited atoms. These observations established that the classical theory was unable to account for the behaviour of small objects. This led to the search for some other theory. Max Planck was the first to suggest a new theory based on the quantum behaviour of energy. When applied to various problems, it was able to account for the experimental observations and hence led to the new theory, named, the quantum theory. In this section, we shall describe how the quantum theory postulated by Planck could explain the experimental observations listed above.

### BLACK-BODY RADIATION

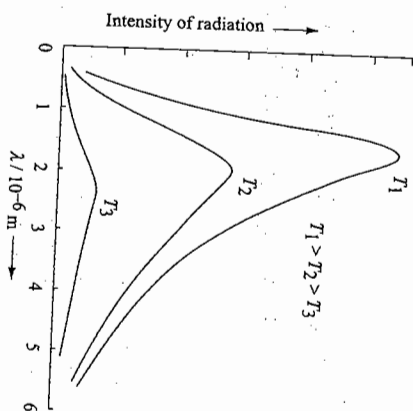
Prior to Max Planck (1901), light was considered to be electromagnetic wave whose energy was proportional to the square of the amplitude of the wave, and was considered to be independent of the frequency of the radiation. This classical theory of radiation was able to explain optical phenomena such as diffraction and scattering. However, when applied to the black-body radiation, this theory could not explain the relative intensities of radiations emitted from a black body when heated to a higher temperature.

A black body is one which can absorb all types of radiation that falls upon it. Experimentally, such a body is best represented by a hollow container with a very small hole in the wall. When such a body is heated, it emits radiations of all types of wavelengths. The origin of radiations from a heated body is the rapid vibrating particles (known as *oscillators*) composing the body. According to Maxwell's electromagnetic theory, these oscillators emit radiant energy in the form of electromagnetic waves. The frequency of the wave emitted from an oscillator is equal to the frequency of the latter. At low temperatures, the emission is mainly in the infrared region, but as the temperature is raised, the wavelength at which most of the light is emitted shifts towards the blue region of the spectrum. The intensity of the emitted radiation depends on the temperature of the container as well as on the wavelength of the radiation. Figure 1.1.1 shows the variation of the intensity of radiation with the wavelength at three different temperatures.

### Classical Theory of Radiation

### Radiations Emitted by a Black Body

Fig. 1.1.1 Variation of intensity of radiation with the wavelength of emitted radiations at three different temperatures



## Two Fundamental Laws of Black-Body Radiations

Based on the classical theory, attempts were made to explain qualitatively and quantitatively the nature of the curves depicted in Fig. 1.1.1. Two fundamental laws regarding the nature of the curves were established. These are described below.

**Stefan-Boltzmann law** This law was established experimentally by Stefan, according to which, the intensity of total radiation  $E$  (the area under the curve) is proportional to the fourth power of the kelvin temperature  $T$ , i.e.

$$E = \sigma T^4 = \left(\frac{4}{c} \sigma\right) T^4 \quad (1.1.1)$$

where  $\sigma$  is a constant, known as the *Stefan's constant*. Its value is found to be  $5.672 \times 10^{-8} \text{ J m}^{-2} \text{ s}^{-1} \text{ K}^{-4}$ . Subsequently, this law was derived by Boltzmann using thermodynamic principles.

**Wien's displacement law** According to this law, the wavelength  $\lambda$  at the maximum of the spectral distribution is inversely proportional to the temperature  $T$ . Thus

$$\lambda_{\text{max}} T = \text{constant} \quad (1.1.2)$$

Theoretical attempts were also made to construct the shape of the energy spectra as a function of wavelength. We describe below the three important attempts in this direction.

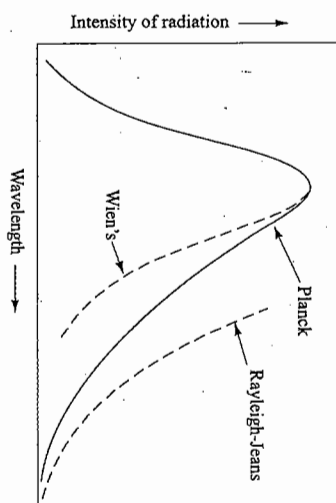
**Wien's contribution** Based on the classical electromagnetic theory and assuming that the oscillators from which the radiations are emitted are of molecular size, Wien was able to obtain the expression

$$E = \frac{a}{\lambda^5} \exp(-b/\lambda T) \quad (1.1.3)$$

where  $E$  is the energy emitted between wavelengths  $\lambda$  and  $\lambda + d\lambda$  and  $a$  and  $b$  are constants.

It was found that the above equation gives very good fitting of experimental curves in the low wavelength region, but fails to reproduce the results at the high wavelength region (Fig. 1.1.2).

Fig. 1.1.2 Graph indicating the fitting of the experimental curve by Wien's law, Rayleigh-Jeans' law and Planck's law



**Rayleigh-Jeans contribution** Applying the classical law of equipartition of

energy (that each vibration mode possesses on an average energy  $\bar{E}$  equal to  $kT$ ) to the oscillators of black body, Rayleigh and Jeans derived Eq. (1.1.6) as follows.

It can be shown that the number of modes of oscillation  $dn$  in the wavelength range  $\lambda$  and  $\lambda + d\lambda$  per unit volume of the cavity is given by

$$dn = \frac{8\pi}{\lambda^4} d\lambda \quad (1.1.4)$$

The energy density in this wavelength region is equal to  $(dn)(\bar{E})$  and is also equal to  $E_\lambda d\lambda$ , where  $E_\lambda$  is the corresponding energy emitted. Thus, we have

$$E_\lambda d\lambda = (dn) \bar{E} \quad (1.1.5)$$

Substituting the expressions of  $dn$  and  $\bar{E}$ , we get

$$E_\lambda d\lambda = \left(\frac{8\pi}{\lambda^4} d\lambda\right) (kT)$$

$$\text{Hence } E_\lambda = \frac{8\pi kT}{\lambda^4} \quad (1.1.6)$$

According to Eq. (1.1.6),  $E_\lambda$  is inversely proportional to the fourth power of the wavelength. Hence,  $E_\lambda$  continues to increase with decreasing  $\lambda$ .

Equation (1.1.6) is found to fit the experimental data at the high wavelength region but fails completely at the low wavelength region and thus leads to what is known as the *ultraviolet catastrophe* (Fig. 1.1.2).

**Planck's contribution** Keeping in view that the Wien's relation was applicable in the low wavelength region and that of Rayleigh-Jeans in the high wavelength region, Planck sought an intermediate expression which could be reduced to the above two laws in the proper range of values of  $\lambda$ . He derived the expression:

$$E_\lambda = \frac{a}{\lambda^5 (\exp(b/\lambda T) - 1)} \quad (1.1.7)$$

**Behaviour of Eq. (1.1.7) at low values of  $\lambda$**  The factor  $\exp(b/\lambda T)$  is very much

greater than one, and thus we may write

$$\exp(b/\lambda T) - 1 \approx \exp(b/\lambda T)$$

With the above relation, Eq. (1.1.7) reduces to

$$E_\lambda = \frac{a}{\lambda^5} \exp(-b/\lambda T)$$

an expression identical to the Wien's relation (Eq. 1.1.3).

**Behaviour of Eq. (1.1.7) at high values of  $\lambda$**  If  $\lambda$  is high, the term  $b/\lambda T$  will have a small value and thus the term  $\exp(b/\lambda T)$  can be written as

$$\exp(b/\lambda T) \approx 1 + \frac{b}{\lambda T}$$

Substituting the above relation in Eq. (1.1.7), we get

$$E_\lambda = \frac{a}{\lambda^5} \frac{1}{\exp(b/\lambda T) - 1} = \frac{a}{\lambda^5} \frac{1}{1 + (b/\lambda T) - 1} = \frac{a}{\lambda^5} \frac{\lambda T}{b}$$

or

$$E_\lambda = \frac{aT}{\lambda^4 b}$$

which is identical to the Rayleigh-Jeans' relation (Eq. 1.1.6) provided  $(a/b) = 8\pi k$ .

After obtaining the expression for the energy distribution in black-body radiation, Planck put forward a theoretical model in order to explain the results. He completely rejected the classical principle of equipartition of energy since this assumption led to the Rayleigh-Jeans expression. Instead, he used the bold assumption that *the oscillator of the black body cannot have any amount of energy but has a discrete energy equal to the integral multiple of some minimum energy  $\epsilon$ , i.e.*

$$\epsilon_i = n\epsilon \quad (1.1.8)$$

where  $\epsilon_i$  is the energy of the  $i$ th oscillator and  $n$  is an integer.

After this, he employed the Boltzmann expression to compute the average energy of the oscillator. According to the Boltzmann law, the number of oscillators having energy  $\epsilon_i$  at temperature  $T$  is given by

$$N_i = n_0 \exp(-\epsilon_i/kT) \quad (1.1.9)$$

where  $n_0$  is a constant. With this expression, the average energy of the oscillator can be computed as follows.

Total number of oscillators,  $N = \sum_i N_i$

Substituting  $N_i$  from Eq. (1.1.9), and by using Eq. (1.1.8), we get

$$\begin{aligned} N &= n_0 + n_0 \exp(-\epsilon/kT) + n_0 \exp(-2\epsilon/kT) + \dots \\ &= n_0 (1 + x + x^2 + \dots) \end{aligned}$$

where  $x = \exp(-\epsilon/kT)$

Equation (1.1.10) can be written as

$$N = \frac{n_0}{1 - x} \quad (1.1.12)$$

since the expansion of  $(1 - x)^{-1}$  gives  $(1 + x + x^2 + \dots)$ .

## Theoretical Model of Planck

## Average Energy of the Oscillator

## Reduction to Rayleigh-Jeans' Relation

## Energy Emitted at Wavelength $\lambda$

Now, the average energy  $\bar{E}$  is given by

$$\bar{E} = \frac{\sum_i (N_i \epsilon_i)}{N}$$

Employing Eqs (1.1.8), (1.1.9) and (1.1.11), we get

$$\begin{aligned} \bar{E} &= \frac{1}{N} [n_0(0) + n_1(\epsilon) + n_2(2\epsilon) + \dots] = \frac{1}{N} [n_0\epsilon(x + 2x^2 + \dots)] \\ &= \frac{1}{N} [n_0\epsilon x(1 + 2x + 3x^2 + \dots)] \end{aligned} \quad (1.1.13)$$

The expression within the bracket is equal to  $1/(1-x)^2$ . It can be proved as follows.

$$(1 + 2x + 3x^2 + \dots) = \frac{d}{dx} (1 + x + x^2 + x^3 + \dots) = \frac{d}{dx} \left( \frac{1}{1-x} \right) = \frac{1}{(1-x)^2}$$

With the above equality, Eq. (1.1.13) becomes

$$\bar{E} = \frac{n_0 \epsilon x / (1-x)^2}{N}$$

which on using Eq. (1.1.12) becomes

$$\bar{E} = \frac{n_0 \epsilon x / (1-x)^2}{n_0 / (1-x)} = \frac{\epsilon x}{1-x}$$

$$\text{i.e. } \bar{E} = \frac{\epsilon \exp(-\epsilon/kT)}{1 - \exp(-\epsilon/kT)} = \frac{\epsilon}{\exp(\epsilon/kT) - 1} \quad (1.1.14)$$

Substituting Eq. (1.1.14) and the expression of  $dn$  in Eq. (1.1.5), we get

$$E_\lambda d\lambda = \left( \frac{8\pi d\lambda}{\lambda^4} \right) \left( \frac{\epsilon}{\exp(\epsilon/kT) - 1} \right) \quad (1.1.15)$$

$$\text{Hence } E_\lambda = \frac{8\pi}{\lambda^4} \left( \frac{\epsilon}{\exp(\epsilon/kT) - 1} \right)$$

Comparing Eqs (1.1.7) and (1.1.15), we have

$$a = 8\pi\epsilon\lambda$$

$$\text{and } \frac{b}{\lambda} = \frac{\epsilon}{k} \quad \text{or} \quad \lambda = \frac{bk}{\epsilon}$$

Eliminating  $\lambda$  in the above two expressions, we have

$$a = (8\pi\epsilon) \left( \frac{bk}{\epsilon} \right)$$

$$\text{or } a = 8\pi bk$$

In Eq. (1.1.15),  $\epsilon$  represents some minimum energy. If it be assumed that  $\epsilon$  is infinitesimally small (in the limit  $\epsilon \rightarrow 0$ ), it can be shown that the present approximation would lead to the classical expression of Rayleigh and Jeans. This is to be expected since the actual energy of an oscillator which is an integral multiple of this infinitesimally smaller energy may then be regarded to vary

continuously—an assumption of the classical theory. In the above approximation, we will have

$$\exp(\epsilon/kT) \approx 1 + \frac{\epsilon}{kT}$$

$$\text{and thus } E_\lambda = \frac{8\pi}{\lambda^4} \left\{ \frac{\epsilon}{1 + (\epsilon/kT) - 1} \right\} = \frac{8\pi kT}{\lambda^4} \quad (\text{Eq. 1.1.6})$$

In order that Eq. (1.1.15) could be reduced to the Wien's relation in the low wavelength region, Planck also took the bold step to state that the *energy*  $\epsilon$  is *directly proportional to the frequency of the radiation*, i.e.

$$\epsilon \propto \nu$$

$$\text{or } \epsilon = h\nu$$

$$(1.1.16)$$

where  $h$  is the Planck's constant and has a value of  $6.6252 \times 10^{-34}$  J s. Since  $\nu = c/\lambda$ , we have

$$\epsilon = \frac{hc}{\lambda} \quad (1.1.17)$$

Substituting Eq. (1.1.17) in Eq. (1.1.15), we have

$$E_\lambda = \frac{8\pi(hc/\lambda)}{\lambda^4 \{\exp(hc/\lambda kT) - 1\}} \quad (1.1.18)$$

Now for low values of  $\lambda$ , we will have

$$\exp(hc/\lambda kT) \gg 1$$

With the above relation, the expression of  $E_\lambda$  is reduced to

$$E_\lambda = \frac{8\pi hc}{\lambda^5} \exp(-hc/\lambda kT) \quad (1.1.19)$$

Comparing the above expression with the Wien's relation (Eq. 1.1.3), we have

$$a = 8\pi hc$$

$$b = \frac{hc}{k}$$

With Eq. (1.1.18), it is possible to reproduce the relative intensities of radiations from a black body as a function of wavelength, both in the low and high wavelength regions of the spectrum (Fig. 1.1.2). The wavelength at which the maximum in the spectral distribution of energy of Fig. 1.1.1 is observed can be computed by differentiating Eq. (1.1.18) with respect to  $\lambda$  and then setting the resultant expression to zero. Starting with the simpler relation given by Eq. (1.1.19), we have

$$\frac{dE_\lambda}{d\lambda} = 8\pi hc \frac{d}{d\lambda} [\lambda^{-5} \exp(-hc/\lambda kT)] = 0$$

or

$$\left[ (-5)(\lambda^{-6}) + \lambda^{-5} \left( \frac{hc}{\lambda^2 kT} \right) \right] \exp(-hc/\lambda kT) = 0$$

### Summary of Planck's Contribution

Thus  $(-5)(\lambda^{-6}) + \frac{hc}{\lambda^2 kT} = 0$   
or  $\lambda T = \frac{hc}{5k} = \text{constant}$   
This expression is, in fact, Wien's displacement law (Eq. 1.1.2).  
Planck's contribution may be summarized as follows:

- In order that the Planck's equation (1.1.7) may be reduced to Rayleigh and Jeans' equation (1.1.6) only in the longer wavelength region, Planck assumed that the oscillator in a black body can exchange energy only by discrete amounts, i.e. the oscillator cannot radiate or absorb any amount of energy but can do so only in small lumps or bundles called quanta.

• In order that the Planck's equation may be reduced to the Wien's equation (1.1.3) only in the low wavelength region, Planck assumed that the energy of the oscillator is directly proportional to its frequency with  $h$  as the constant of proportionality. This constant is called *Planck's constant* and it has to have a finite value. The value of  $h$  cannot be zero since this would lead to the classical theory of continuous energy distribution.

### Problem 1.1.1

Starting from Planck's radiation law, obtain the Stefan-Boltzmann law  $E = \sigma T^4$  where  $E$  is the total radiation energy from  $\lambda = 0$  to  $\lambda = \infty$ , i.e.

$$E = \int_0^\infty E_\lambda d\lambda = \sigma T^4 \quad \text{Given: } \int_0^\infty \frac{x^3 dx}{(e^x - 1)} = \frac{\pi^4}{15}$$

The Planck's equation is

$$E_\lambda = \frac{8\pi hc}{\lambda^5 \{\exp(hc/\lambda kT) - 1\}}$$

Let  $x = hc/\lambda kT$ . Therefore

$$\lambda = hc/xkT \quad \text{and} \quad d\lambda = -hc dx/x^2 kT$$

Substituting the above relations in the Planck's equation, we get

$$E_\lambda = \frac{8\pi hc}{(hc/xkT)^5 (e^x - 1)}$$

$$\text{Thus } E_\lambda d\lambda = \frac{8\pi hc}{(hc/xkT)^5 (e^x - 1)} \left( -\frac{hc dx}{x^2 kT} \right) = E_x dx$$

Integrating the above expression from 0 to  $\infty$ , we have

$$E = \int_0^\infty E_\lambda d\lambda = \int_0^\infty E_x dx = \int_0^\infty \frac{8\pi hc}{(hc/xkT)^5 (e^x - 1)} \left( -\frac{hc}{x^2 kT} \right) dx$$

$$\begin{aligned}
 &= - \int_0^\infty \frac{8\pi x^3 k^4 T^4}{(hc)^3 (e^x - 1)} dx = - \frac{8\pi k^4 T^4}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1} dx \\
 &= - \frac{8\pi k^4 T^4}{(hc)^3} \left( -\frac{\pi^4}{15} \right) = \frac{8\pi^5 k^4}{15(hc)^3} T^4 \\
 &= \sigma T^4
 \end{aligned}$$

where  $\sigma = 8\pi^5 k^4 / 15(hc)^3$ .

### THE PHOTOELECTRIC EFFECT

The Planck's statement that the oscillators in a black body radiate energy in elementary discrete units was extended by Einstein to the extent that the radiation field itself is quantized, consisting of light quanta called *photons*. Thus, Einstein considered the light wave to be corpuscular in nature with each photon carrying an energy equal to  $h\nu$ . With the corpuscular nature of light, he was successful in interpreting the photoelectric effect.

In the photoelectric effect, the electrons are emitted instantaneously from a clean metal plate in vacuum when a beam of light falls on it. The following characteristics are observed:

- The electrons are emitted instantaneously from a given metal plate when it is irradiated with radiation of frequency equal to or greater than some minimum frequency, called the *threshold frequency*.
- The kinetic energy of the emitted electrons depends on the frequency of the incident radiation and not on its intensity. The kinetic energy of electrons increases linearly with increase in the frequency of the incident radiation.
- The number of electrons emitted is proportional to the intensity of the incident radiation.

The electron in a metal possesses potential energy (PE) which must be supplied before an electron can be removed from the metal. This energy, known as the *work function*, is the ionization energy (IE) of the metal. If the emitted electron carries some kinetic energy (KE), the total energy supplied to the electron is equal to the sum of its potential energy and kinetic energy.

In the classical theory, the energy of the light beam depends on its intensity. Thus, a continuous exposure of the metal with light causes the electron to gain more and more energy from the light and ultimately a stage would be reached when it has acquired sufficient energy to cause its ionization. Hence, it is expected that there might exist a time interval between the exposure of the metal and the emission of electron. This time interval may be decreased by increasing the intensity of the light. Thus, the classical theory of light cannot explain the characteristics of photoelectric effect listed above, viz., the instantaneous emission

of electrons, existence of threshold frequency and the dependence of kinetic energy of the emitted electron on the frequency of the light.

According to Einstein, the above characteristics can be explained by employing Planck's idea of quantization of energy. Thus, light may be considered to be made up of discrete particles called photons. Each photon carries an energy equal to  $h\nu$ . When this photon collides with the electron of the metal, the electron acquires energy equal to the energy of the photon. Thus, the energy of the emitted electron is given by

$$h\nu = \text{KE} + \text{PE} = \frac{1}{2} m v^2 + \text{IE} \quad (1.1.20)$$

If the incident radiation is of threshold frequency, the electron will be emitted without any kinetic energy. In this case, we have

$$h\nu_0 = \text{IE} \quad (1.1.21)$$

It is obvious that if the frequency of the light is smaller than  $\nu_0$ , the electron will not acquire sufficient energy to cause its ionization.

From Eq. (1.1.20), it follows that the kinetic energy of electrons depends on the frequency of incident radiation and not on the intensity of light. By the term intensity of light, we mean the number of quanta striking the metal per unit time. This will have an effect only on the number of electrons emitted and not on their kinetic energy. Thus, the number of electrons emitted increases with increase in the intensity of light.

Combining Eqs (1.1.20) and (1.1.21), we have

$$h\nu = \text{KE} + h\nu_0 \quad \text{or} \quad \text{KE} = h\nu - h\nu_0 \quad (1.1.22)$$

From Eq. (1.1.22), it may be concluded that the kinetic energy of the emitted electrons varies linearly with the frequency of the incident radiation. A plot of kinetic energy of the emitted electrons versus frequency of the incident radiation yields a straight line with slope equal to the Planck's constant  $h$  (Fig. 1.1.3). This provides one of the methods to determine the value of Planck's constant.

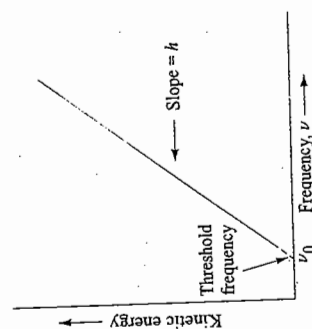


Fig. 1.1.3 Variation of kinetic energy of the emitted electrons with the frequency of the incident radiation

### Characteristics of Photoelectric Effect

### Energy Requirement for the Emission of Electrons

### Failure of Classical Theory to Explain Photoelectric Effect

### Experimental Determination of Kinetic Energy of Emitted Electrons

The kinetic energy of emitted electrons can be determined with a device shown in Fig. 1.1.4. In this method, a retarding voltage is applied and its value is steadily increased till no electrons from the metal plate reach the collector plate (Fig. 1.1.5).

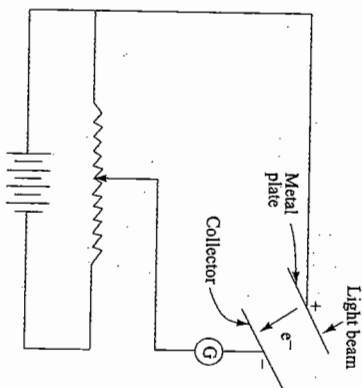
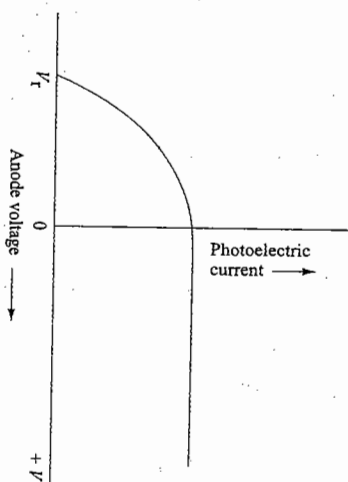


Fig. 1.1.4 Experimental device to determine the kinetic energy of the emitted electrons

Fig. 1.1.5 Decrease of photoelectric current with the retarding potential



The electrical work done in the above process is  $V_r e$ , where  $V_r$  is the retarding voltage and  $e$  is the electronic charge. The electrical work will be equal to the kinetic energy of the electrons. Thus, we have

$$V_r e = \frac{1}{2} m v^2 = h\nu - h\nu_0 \quad (1.1.23)$$

### Example 1.1.1

- (a) Calculate the kinetic energy of a photoelectron emitted by a sodium surface when light of wavelength 400 nm is incident on it. The work function of sodium is 2.28 eV.  
(b) Calculate the value of the longest wavelength which can result in the emission of a photoelectron from a sodium surface.

(a) Energy of the incident photon is

$$E_1 = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m s}^{-1})}{(400 \times 10^{-9} \text{ m})} = 4.969 \times 10^{-19} \text{ J}$$

### Solution

The work function of sodium is

$$E_2 = 2.28 \text{ eV} \approx (2.28 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV}) \\ = 3.653 \times 10^{-19} \text{ J}$$

Energy carried by the electron is

$$E_3 = E_1 - E_2 = 4.969 \times 10^{-19} \text{ J} - 3.653 \times 10^{-19} \text{ J} = 1.316 \times 10^{-19} \text{ J}$$

- (b) Wavelength of the incident photon just sufficient to knock out the electron is

$$\lambda = \frac{hc}{\text{work function}} = \frac{(6.626 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m s}^{-1})}{(3.653 \times 10^{-19} \text{ J})} \\ = 5.441 \times 10^{-7} \text{ m} = 544.1 \text{ nm}$$

### HEAT CAPACITY

#### Heat Capacity Based on the Law of Equipartition of Energy

Einstein also showed that the problem of variation of heat capacity of monatomic solids with temperature can be resolved by employing Planck's idea of quantization. The monatomic solid may be considered a collection of oscillators with three vibrational degrees of freedom. On the basis of the classical law of equipartition of energy, each oscillator of such a solid possesses an average energy equal to  $3kT$ . Thus, for one mole of oscillators, the molar energy is

$$E = N_A(3kT) = 3RT \quad (1.1.24)$$

Since  $C_V = (\partial E / \partial T)_V$ , we have

$$C_V = 3R \quad (1.1.25)$$

According to Eq. (1.1.25), monatomic solids have a constant heat capacity equal to  $3R$  (a value which was obtained empirically by Dulong and Petit). Experimentally, it is found that this value of heat capacity is observed only at high temperatures.

#### Disagreement with Experimental Fact

According to the classical theory, the heat capacity of a monatomic solid should be independent of temperature. This conclusion, however, does not agree with the experimental findings, according to which the heat capacity decreases with the decrease in temperature. Figure 1.1.6 depicts such variations for Pb, Cu, Si and C.

#### Einstein Explanation of Variation of Heat Capacity

By employing Planck's idea of quantization, Einstein was able to explain the variation of heat capacity with temperature. He assumed that the oscillator can have vibrational energy which is an integral multiple of some minimum value, i.e.

$$E = n\varepsilon \quad (1.1.26)$$

or  $\varepsilon = n\nu_0$

where  $\nu$  is the frequency of the oscillator and  $\nu_0$  is the smallest allowed frequency. Thus, all oscillators are not vibrating with the same frequency but have values which are simply an integral multiple of the smallest frequency  $\nu_0$ . The number of oscillators possessing the frequency  $\nu$  can be determined from Boltzmann law (Eq. 1.1.9).



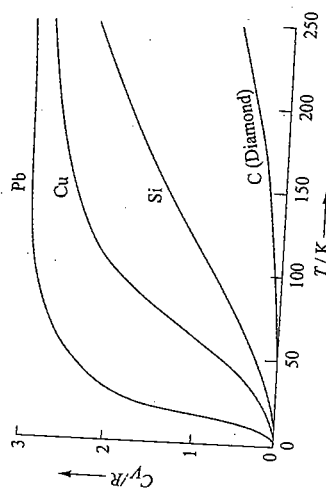


Fig. 1.1.6 The variation of molar heat capacity with temperature for Pb, Cu, Si and C

The average energy of the oscillators as given by Eq. (1.1.14) is

$$\bar{\epsilon} = \frac{\epsilon}{\exp(\epsilon/kT) - 1}$$

Substituting  $\epsilon = h\nu_0$ , we get

$$\bar{\epsilon} = \frac{h\nu_0}{\exp(h\nu_0/kT) - 1}$$

The molar energy of a solid is

$$E = N_A(3\bar{\epsilon}) = N_A \left\{ 3 \frac{h\nu_0}{\exp(h\nu_0/kT) - 1} \right\} \quad (1.1.27)$$

and the corresponding value of molar heat capacity is

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = 3N_A k \left( \frac{h\nu_0}{kT} \right)^2 \frac{\exp(h\nu_0/kT)}{\{\exp(h\nu_0/kT) - 1\}^2} \quad (1.1.28)$$

Equation (1.1.29) is known as *Einstein equation*.

At low temperatures, we have

$$h\nu_0 \gg kT$$

and thus  $\exp(h\nu_0/kT) \gg 1$ . Under these conditions, Eq. (1.1.29) will reduce to

$$C_V = 3N_A k \left( \frac{h\nu_0}{kT} \right)^2 \exp(-h\nu_0/kT) \quad (1.1.30)$$

On decreasing the temperature, the exponential factor decreases much faster than the corresponding increase in the factor  $(h\nu_0/kT)^2$ . Consequently,  $C_V$  decreases with decrease in temperature. Einstein suggested that the above decrease is basically due to the lesser absorption of energy by the oscillators at low temperatures. This is so because the oscillators can absorb energy in units of  $h\nu_0$  and the value of  $kT$  is much smaller as compared to  $h\nu_0$ .

The value of  $\nu_0$  is different for different solids. The temperature at which the decrease in heat capacity becomes important depends upon the value of  $\nu_0$  of the solid. If we assume the oscillators to be harmonic, then

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k_f}{m}}$$

where  $k_f$  is the Hooke's law constant of the oscillator and  $m$  is its mass (see Section 1.5). It is obvious that the value of  $\nu_0$  will be larger for more strongly bound atoms in the solid ( $k_f$  larger) and for the lighter atoms ( $m$  smaller). Thus, solid with these characteristics will have a high temperature at which the heat capacity will increase to the classical value of  $3R$ .

It can be shown that the Einstein equation (1.1.29) can be reduced to the classical value of  $3R$  at temperatures that are high enough so that the factor  $h\nu_0$  is much less than  $kT$ . Equation (1.1.29) is

$$C_V = 3N_A k \left( \frac{h\nu_0}{kT} \right)^2 \frac{\exp(h\nu_0/kT)}{\{\exp(h\nu_0/kT) - 1\}^2}$$

Expanding the exponential factor, we have

$$C_V = 3N_A k \left( \frac{h\nu_0}{kT} \right)^2 \left[ \frac{1 + (h\nu_0/kT) + \dots}{\left\{ 1 + (h\nu_0/kT) + \frac{1}{2} (h\nu_0/kT)^2 + \dots - 1 \right\}^2} \right]$$

$$\text{or } C_V = 3N_A k \frac{(h\nu_0/kT)^2 + (h\nu_0/kT)^3 + \dots}{\left\{ (h\nu_0/kT) + \frac{1}{2} (h\nu_0/kT)^2 + \dots \right\}^2}$$

At sufficiently high values of  $T$ ,  $h\nu_0/kT$  is very small and the terms with powers higher than two can be neglected. Thus, we have

$$C_V = 3N_A k = 3R$$

### THE BOHR MODEL OF ATOM

Planck's idea of quantization of energy was applied by Bohr to the problem of hydrogen spectra. Experimentally, it was found by Balmer that the wavelengths of emitted radiations in the visible and near-ultraviolet spectrum of hydrogen could be expressed as

$$\lambda/\text{nm} = 364.56 \left( \frac{n_2^2}{n_2^2 - n_1^2} \right) \quad (1.1.31)$$

where  $n_1$  and  $n_2$  are integer constants. The constant  $n_1$  has a fixed value of 2 whereas  $n_2$  has any integral value greater than 2, i.e. 3, 4, 5, .... For example, the observable spectral lines in the Balmer series at 656.21 nm, 486.07 nm, 434.0 nm and 410.13 nm of the hydrogen spectra can be reproduced by the above formula as

### Limiting Value of $C_V$ at Higher Temperatures

### Experimental Findings by Balmer about Hydrogen Spectra

### Limiting Value of $C_V$ at Lower Temperatures

shown in the following.

$$\lambda_1/\text{nm} = 656.21 = 364.56 \left( \frac{3^2}{3^2 - 2^2} \right) = 364.56 \left( \frac{9}{5} \right) = 656.21$$

$$\lambda_2/\text{nm} = 486.07 = 364.56 \left( \frac{4^2}{4^2 - 2^2} \right) = 364.56 \left( \frac{16}{12} \right) = 486.08$$

$$\lambda_3/\text{nm} = 434.00 = 364.56 \left( \frac{5^2}{5^2 - 2^2} \right) = 364.56 \left( \frac{25}{21} \right) = 434.00$$

and  $\lambda_4/\text{nm} = 410.13 = 364.56 \left( \frac{6^2}{6^2 - 2^2} \right) = 364.56 \left( \frac{36}{32} \right) = 410.13$

Expressing Eq. (1.1.31) in the frequency unit, we have

$$\begin{aligned} \nu &= \frac{c}{\lambda} = \frac{c}{(364.56 \times 10^{-9} \text{ m}) \left[ \frac{n_2^2}{n_1^2} - 1 \right]} \\ &= \frac{c}{(364.56 \times 10^{-9} \text{ m})} \frac{n_2^2 - n_1^2}{n_2^2} = \frac{c}{(364.56 \times 10^{-9} \text{ m})} \left( 1 - \frac{n_1^2}{n_2^2} \right) \\ &= \frac{c}{(364.56 \times 10^{-9} \text{ m})} n_1^2 \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \end{aligned}$$

Since  $n_1 = 2$ , we have

$$\nu = \frac{4c}{(364.56 \times 10^{-9} \text{ m})} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

or  $\nu = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$  (1.1.32)

Equation (1.1.32) was suggested by Ritz. The constant  $R_H$  is known as the Rydberg constant for hydrogen and has a value of  $3.28983 \times 10^{15} \text{ Hz}$  ( $1.09737 \times 10^7 \text{ cm}^{-1}$ ).

In the Rutherford model of the atom, electrons revolve around the nucleus in such a way that the Coulombic attraction of the electron by the nucleus is balanced by the centrifugal force which tends to pull the electron and nucleus apart, i.e., attractive (centripetal) force = centrifugal force

$$\frac{(Ze)(e)}{(4\pi\epsilon_0)r^2} = \frac{mv^2}{r} \quad (1.1.33)$$

where  $e$  is the electronic charge. All other symbols have their usual meanings. According to Eq. (1.1.33), the electron can revolve in an orbit which can be at any distance from the nucleus, i.e.,  $r$  can have any value. For a given value of  $r$ , the velocity with which an electron moves in the orbit can be calculated from Eq. (1.1.33). Since  $r$  can vary in a continuous manner, the velocity of the electron can also vary in a continuous manner.

### Instability of Rutherford Model of Hydrogen Atom

### Bohr Model of Hydrogen Atom

The model of atom in which the electrons move in orbits around positively charged nucleus would have to be reconciled with the principles of classical electrodynamics, according to which a negative charge revolving around a positive charge experiences a continuous acceleration and thereby should radiate continuous energy. By losing energy continuously, the electron would come nearer and nearer to the nucleus and eventually would fall in the nucleus. Thus, it gives rise to an unstable atom—a conclusion which contradicts the experimental observations (as atom is quite stable) and moreover, such a model would give rise to continuous spectra instead of the experimentally determined discrete spectra.

Bohr resolved the above problem by introducing Planck's idea of quantization of energy. The first thing which Bohr concluded was that the classical electrodynamics did not adequately represent systems of atomic dimensions and, therefore, it has to be set aside. His model of atomic structure involved the following postulates.

- The electron in an atom can revolve around the nucleus only in certain allowed circular orbits without losing any energy.
- The electron can jump from one of the allowed orbits to another and can thereby gain or lose energy equivalent to the difference in the energy of the two involved orbits. Thus, when it jumps from a higher energy orbit to a state of lower energy, the electron loses energy which appears in the form of radiation of frequency  $\nu$  such that  $h\nu$  is equal to the difference in the energies of the two states.

Bohr showed that the allowed stationary orbits can be generated by imposing the quantum restriction on the classical expression given by Eq. (1.1.33) of the Rutherford's model. The quantum restriction proposed by Bohr was that the angular momentum of the revolving electron is an integral multiple of the basic unit of momentum ( $h/2\pi$ ), i.e.,

$$m\nu r = n \left( \frac{h}{2\pi} \right) \quad (1.1.34)$$

where  $n$  is the number of quanta of angular momentum and is known as the quantum number.† The number  $n$  can have only integral values 1, 2, 3, ....

† This quantum restriction was derived by Bohr from his postulate that the binding energy of an electron rotating in an orbit of an atom is given by the expression

$$W = nh\nu/2$$

where  $n$  has integral values and  $\omega$  is the angular frequency of rotation of the electron in an orbit of an atom. The angular momentum expression in terms of frequency of rotation is given by

$$\begin{aligned} L &= m\nu r = m\nu \left( \frac{v}{2\pi\omega} \right) \quad (\text{since } v = 2\pi r\omega) \\ &= \left( \frac{1}{2} m\nu^2 \right) \left( \frac{1}{\pi\omega} \right) = \frac{T}{\pi\omega} \end{aligned}$$

Now since the kinetic energy  $T$  is equal to the binding energy  $W$ , we have

$$L = \frac{W}{\pi\omega} = \frac{1}{\pi\omega} \left( \frac{nh\omega}{2} \right) = n \left( \frac{h}{2\pi} \right)$$

### Radius of Stationary Orbits

The allowed stationary orbits can be obtained by eliminating  $v$  from Eqs (1.1.33) and (1.1.34). From Eq. (1.1.34), we have

$$v = \frac{nh}{2\pi mr}$$

Substituting the above expression in Eq. (1.1.33), we get

$$\frac{Ze^2}{(4\pi\epsilon_0)r^2} = \frac{m}{r} \left( \frac{nh}{2\pi mr} \right)^2 = \frac{n^2 h^2}{4\pi^2 m r^3}$$

Cancelling  $r^2$ , we have

$$\frac{Ze^2}{4\pi\epsilon_0} = \frac{n^2 h^2}{4\pi^2 m r}$$

$$\text{or } r = \frac{n^2 h^2 (4\pi\epsilon_0)}{4\pi^2 m Ze^2} = \frac{n^2}{Z} a_0 \quad (1.1.35)$$

$$\text{where } a_0 = \frac{h^2 (4\pi\epsilon_0)}{4\pi^2 m e^2} \quad (1.1.36)$$

The quantity  $a_0$ , known as Bohr radius, has a constant value since all the quantities on the right side of Eq. (1.1.36) are constants. Its value may be calculated as follows.

$$\begin{aligned} a_0 &= \frac{h^2}{4\pi^2 m} \frac{4\pi\epsilon_0}{e^2} \\ &= \frac{(6.626 \times 10^{-34} \text{ J s})^2}{4(3.1416)^2 (9.109 \times 10^{-31} \text{ kg})} \\ &\quad \times \left\{ \frac{(4)(3.141)(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})}{(1.6022 \times 10^{-19} \text{ C})^2} \right\} \\ &= 0.529 \times 10^{-10} \text{ m} = 52.9 \text{ pm} \end{aligned}$$

### Comment on the Radii of Bohr Orbits

From Eq. (1.1.35), it follows that *only certain orbits are allowed* since the quantum number  $n$  can have only integral values 1, 2, 3, .... The smallest Bohr radius for a hydrogen atom is equal to  $a_0$ , since  $n = 1$  and  $Z = 1$ . The radii of other orbits are simply  $n^2$  times the value of  $a_0$ . Thus, the second orbit has a radius which is four times that of the first orbit, the third orbit, nine times, fourth orbit, sixteen times and so on (Fig. 1.1.7).

### Energy of Electron in a Stationary Orbit

The total energy of the electron in any orbit consists of two terms, viz., energy due to its motion (kinetic energy, represented by the symbol  $T$ ) and energy by virtue of its position relative to the nucleus (potential energy, represented as  $V$ ). Thus, we have

$$\begin{aligned} E &= T + V \\ &= \frac{1}{2} m v^2 - \frac{Z e^2}{(4\pi\epsilon_0)r} \quad (1.1.37) \end{aligned}$$

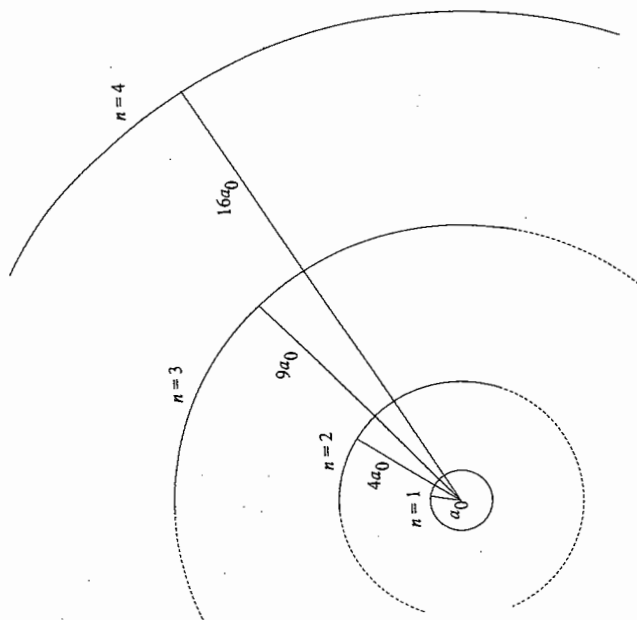


Fig. 1.1.7 Bohr's orbits in hydrogen atom

From Eq. (1.1.33), we have

$$m v^2 = \frac{Z e^2}{(4\pi\epsilon_0)r}$$

Substituting this in Eq. (1.1.37), we have

$$E = \frac{1}{2} \frac{Z e^2}{(4\pi\epsilon_0)r} - \frac{Z e^2}{(4\pi\epsilon_0)r} = -\frac{1}{2} \frac{Z e^2}{(4\pi\epsilon_0)r} \quad (1.1.38)$$

Substituting the expression of  $r$  from Eq. (1.1.35), we have

$$\begin{aligned} E &= -\frac{1}{2} \frac{Z e^2}{(4\pi\epsilon_0) \left\{ \frac{n^2 h^2 (4\pi\epsilon_0)}{4\pi^2 m Z e^2} \right\}} \\ E &= -\frac{1}{n^2} \left\{ \frac{2\pi^2 m Z^2 e^4}{h^2 (4\pi\epsilon_0)^2} \right\} \quad (1.1.39) \end{aligned}$$

Since  $n$  can have only integral values, it follows that the total energy of the electron is also quantized. The negative sign in Eq. (1.1.39) tells that the electron is bound to the nucleus. The electron has a minimum energy when it occupies the lowest allowed orbit (i.e.  $n = 1$ ) and its energy increases as  $n$  becomes larger and larger. The electron can have zero value of maximum energy when  $n = \infty$ . The zero energy means that the electron is no longer bound to the nucleus.

### Comment on Energies

### Energy Expression for the Spectral Lines

Now according to the Bohr postulate, the atom can emit radiations only when the electron jumps from an orbit of higher energy to one of lower energy. This amounts to a jump from an orbit of higher quantum number ( $n_2$ ) to the orbit of lower quantum number ( $n_1$ ). The energy difference would be

$$\begin{aligned}\Delta E &= E_{n_2} - E_{n_1} \\ &= \frac{2\pi^2 m Z^2 e^4}{h^2 (4\pi\epsilon_0)^2} \left( -\frac{1}{n_2^2} + \frac{1}{n_1^2} \right) = \frac{2\pi^2 m Z^2 e^4}{h^2 (4\pi\epsilon_0)^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)\end{aligned}$$

For the hydrogen atom  $Z = 1$ , and thus

$$\Delta E = \frac{2\pi^2 m e^4}{h^2 (4\pi\epsilon_0)^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Writing this in the frequency unit, we have

$$\begin{aligned}\nu &= \frac{\Delta E}{h} = \frac{2\pi^2 m e^4}{h^3 (4\pi\epsilon_0)^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ &= R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (1.1.40)\end{aligned}$$

where  $R_H = 2\pi^2 m e^4 / h^3 (4\pi\epsilon_0)^2$ . This equation is, in fact, the Ritz equation (Eq. 1.1.32).

Bohr's theory identifies the Rydberg constant with the other fundamental constants, the value of which is calculated in the following.

$$\begin{aligned}R_H &= \frac{2\pi^2 m e^4}{h^3 (4\pi\epsilon_0)^2} \\ &= \frac{2(3.1416)^2 (9.1095 \times 10^{-31} \text{ kg})}{(6.626 \times 10^{-34} \text{ J s})^3}\end{aligned}$$

$$\begin{aligned}&\times \left[ \frac{(1.6022 \times 10^{-19} \text{ C})^4}{\{4(3.1416)(8.8542 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})\}^2} \right] \\ &= 3.2902 \times 10^{15} \text{ s}^{-1}\end{aligned}$$

In terms of wavenumber, we have

$$\tilde{\nu}_{R_H} = \frac{3.2902 \times 10^{15} \text{ s}^{-1}}{2.9979 \times 10^8 \text{ m s}^{-1}} = 1.0972 \times 10^7 \text{ m}^{-1}$$

The value of  $\tilde{\nu}_{R_H}$  is very close to the experimental value of  $1.09737 \times 10^5 \text{ cm}^{-1}$ .

Five spectral series of atomic hydrogen are known. These are:

Lyman series	Lies in the ultraviolet spectral region.
Balmer series	Lies in the visible region.
Paschen series	Lies near infrared region.
Brackett series	Lies in the infrared region.
Pfund series	Lies in the far infrared region.

### Spectral Series Shown by Hydrogen Atom

These spectral lines can be generated from Eq. (1.1.40) by giving different values to  $n_1$  and  $n_2$ . Thus, we have

Lyman series	$n_1 = 1,$	$n_2 = 2, 3, 4, \dots$
Balmer series	$n_1 = 2,$	$n_2 = 3, 4, 5, \dots$
Paschen series	$n_1 = 3,$	$n_2 = 4, 5, 6, \dots$
Brackett series	$n_1 = 4,$	$n_2 = 5, 6, 7, \dots$
Pfund series	$n_1 = 5,$	$n_2 = 6, 7, \dots$

These are also shown in Fig. 1.1.8.

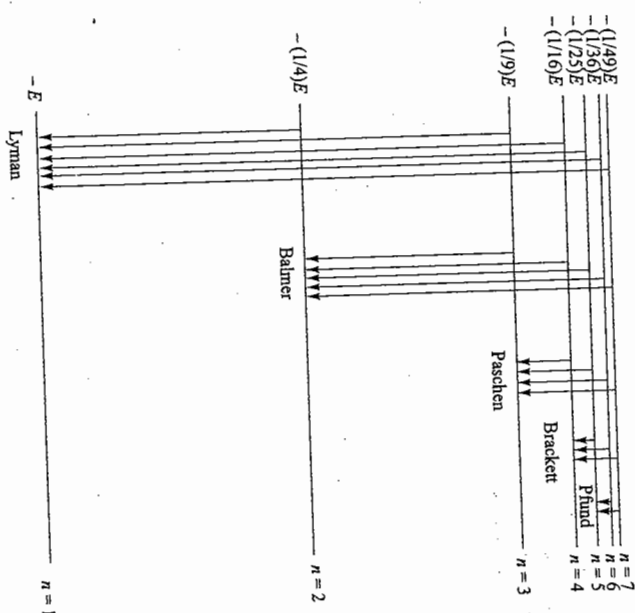


Fig. 1.1.8 A representation of the observed spectral lines of the hydrogen atom

### Limitations of Bohr's Theory

At the end some remarks about the Bohr's theory may be made. The Bohr's theory was abandoned twelve years after its formulation in favour of the present quantum theory of atomic structure. Bohr by introducing quantization of angular momentum was able to explain the spectral lines of hydrogen atom. His theory can very well account for the spectral lines for the hydrogenic species—species containing one electron such as  $\text{He}^+$  and  $\text{Li}^{2+}$ . Bohr's theory, however, completely failed when applied to atoms containing more than one electron. Besides these, Bohr's theory provides no explanation for the relative intensities of the various spectral lines about the splitting of spectral line into many lines in the presence of a magnetic field (Zeeman effect) and an electrical field (Stark effect).

### Correction for the Finite Mass of the Nucleus

So far in the Bohr's theory, we have assumed that the nucleus is at rest and the electron is revolving around it. However, this assumption of the nucleus to be at rest is entirely valid only if the mass of the nucleus is infinite. Because of the finite mass of the nucleus, both the nucleus and the electron are revolving around a common centre of mass which lies on the line connecting the two particles, as shown in Fig. 1.1.9. In view of this, Bohr's theory needs to be corrected.

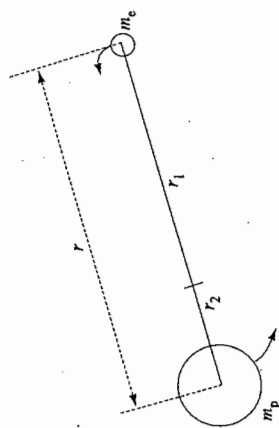


Fig. 1.1.9 Electron and the nucleus revolving around a common centre of mass

It can be shown that the entire formalism of Bohr's theory remains unaltered even if the above feature of revolving nucleus and electron around the common centre of mass is considered. The only change to be made is to replace the mass of electron  $m_e$  by the reduced mass of the atom, defined as

$$\mu = \frac{m_p m_e}{m_p + m_e}$$

This may be proved as follows.

The linear velocity  $v$  of a particle revolving around a point can be expressed in terms of its angular velocity  $\omega$  by an expression<sup>†</sup>

$$v = \omega r \quad (1.1.41)$$

Now the orbital angular momentum of the electron

$$= m_e v r = m_e r^2 \omega \quad (1.1.42)$$

For the entire atom, the total orbital angular momentum is equal to the sum of the orbital angular momenta for the electron of mass  $m_e$  and for the proton of mass  $m_p$ . Thus, we have

$$L = m_e r_1^2 \omega + m_p r_2^2 \omega \quad (1.1.43)$$

where the angular velocity  $\omega$  is the same for both electron and proton. The distances  $r_1$  and  $r_2$  can be expressed in terms of the distance  $r$  between the proton and the

<sup>†</sup> By definition,  $\omega$  is expressed in radians/second. In one revolution, the particle covers a distance of  $2\pi r$  and traverses an angle of  $2\pi$  radians. If  $\nu$  is the frequency of rotation (number of cycles/second), it follows that

$$\nu = (2\pi r)\nu \quad \text{and} \quad \omega = (2\pi)\nu$$

Hence

$$v = \omega r$$

electron. From the location of centre of mass, we have

$$m_e r_1 = m_p r_2$$

Combining this with the relation  $r = r_1 + r_2$ , we have

$$r_1 = \frac{m_p}{m_p + m_e} r \quad \text{and} \quad r_2 = \frac{m_e}{m_e + m_p} r$$

Thus, Eq. (1.1.42) modifies to

$$\begin{aligned} L &= m_e \left( \frac{m_p}{m_e + m_p} r \right)^2 \omega + m_p \left( \frac{m_e}{m_e + m_p} r \right)^2 \omega \\ &= \left( \frac{m_e m_p}{m_e + m_p} \right) r^2 \omega \end{aligned} \quad (1.1.44)$$

$$\text{or} \quad L = \mu r^2 \omega = I \omega$$

where  $I$  is the moment of inertia of the molecule. In a similar manner, it can be shown that the expressions corresponding to the kinetic energy and centrifugal force are

$$\text{KE} = \frac{1}{2} \mu (r\omega)^2 = \frac{1}{2} I \omega^2 \quad (1.1.45)$$

$$\text{Centrifugal force} = \frac{\mu (r\omega)^2}{r} = \frac{I \omega^2}{r}$$

Comparing Eq. (1.1.44) with Eq. (1.1.42), we observe that the orbital angular momentum of a system involving the revolution of two particles (interparticle distance  $r$ ) can be obtained from the corresponding expression for a single revolving particle by simply replacing the mass  $m$  by the reduced mass  $\mu$  and linear velocity of the particle by  $r$  times its angular velocity. Comparison of Eqs (1.1.45) and (1.1.46) with those for the single particle also leads to the same conclusion. In other words, we can say that the system involving the revolution of two particles may be replaced by a hypothetical, but mathematically equivalent, model in which one of the particles (heavier one) is at rest and the other is revolving around it with a mass of  $\mu$  instead of  $m$ .

Now the correction to Bohr's theory can be made by simply replacing the mass of electron  $m_e$  by the reduced mass  $\mu$ . Thus, the corrected expressions are

$$E = - \frac{2\pi^2 \mu e^4}{n^2 h^2 (4\pi\epsilon_0)^2}$$

$$r = \frac{n^2 h^2 (4\pi\epsilon_0)}{4\pi^2 \mu e^2} = n^2 a_0$$

$$\text{where } a_0 = \frac{h^2 (4\pi\epsilon_0)}{4\pi^2 \mu e^2}$$

$$\text{and } \tilde{\nu} = \frac{2\pi^2 \mu e^4}{ch^3 (4\pi\epsilon_0)^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

**Example 1.1.2**

Calculate the speed of an electron in the first Bohr orbit of the hydrogen atom.

Given:  $a_0 = 52.9$  pm.

We have

$$v = n \left( \frac{h}{2\pi} \right) \frac{1}{mr}$$

For the first Bohr orbit  $n = 1$ . Hence

$$v = (1) \frac{(6.626 \times 10^{-34} \text{ J s})}{(2)(3.1416)(9.1095 \times 10^{-31} \text{ kg})(52.9 \times 10^{-12} \text{ m})} = 2.188 \times 10^6 \text{ m s}^{-1}$$

**Example 1.1.3****Solution**

Calculate the ionization energy of the hydrogen atom.

The ionization of an atom is the energy required to knock out the electron completely from the atom to give a positive ion. Thus, in this case we have

$$n_1 = 1 \text{ and } n_2 = \infty$$

$$\text{Hence, } \Delta E = \frac{2\pi^2 m}{h^2} \left( \frac{e^4}{(4\pi\epsilon_0)^2} \right) \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = \frac{2\pi^2 m}{h^2} \left( \frac{e^4}{(4\pi\epsilon_0)^2} \right)$$

Substituting the values, we have

$$\Delta E = \frac{2(3.1416)^2(9.1095 \times 10^{-31} \text{ kg})}{(6.626 \times 10^{-34} \text{ J s})^2} \left[ \frac{(1.6022 \times 10^{-19} \text{ C})^4}{\{4(3.1416)(8.8542 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})\}^2} \right] = 2.18 \times 10^{-18} \text{ J}$$

**Example 1.1.4****Solution**

Calculate in eV the third ionization potential of the lithium atom.

The third ionization potential means to knock out the last single electron from the  $\text{Li}^{2+}$  ion, i.e.  $\text{Li}^{2+} \rightarrow \text{Li}^{3+} + e^-$ . In this case,  $Z = 3$  and thus, we have

$$\Delta E = 9 \left( \frac{2\pi^2 m}{h^2} \right) \left( \frac{e^4}{(4\pi\epsilon_0)^2} \right)$$

Using the result of Example 1.1.3, we get

$$\Delta E = 9 \times 2.18 \times 10^{-18} \text{ J} = 1.962 \times 10^{-17} \text{ J}$$

Since  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ , we have

$$\Delta E/\text{eV} = \frac{1.962 \times 10^{-17}}{1.602 \times 10^{-19}} = 122.4$$

**1.2 TOWARDS THE WAVE NATURE OF THE ELECTRON****Wave-Particle Duality**

Electromagnetic radiations which were considered to have wave characteristics, also possess particle characteristics. The converse of the above aspect, viz., all material particles, whether big or small, possess the wave characteristics, was proposed by de Broglie. The relation connecting the characteristics of wave and particle nature of radiation may be derived as follows.

Both the wave and particle nature of the radiation are associated with the energy according to the following relations.

$$\text{Planck's relation} \quad E = h\nu = \frac{hc}{\lambda} \quad (1.2.1)$$

$$\text{Einstein's relation} \quad E = mc^2 \quad (1.2.2)$$

Equating Eqs (1.2.1) and (1.2.2), we obtain the relation

$$mc^2 = \frac{hc}{\lambda} \quad \text{or} \quad mc = \frac{h}{\lambda} \quad (1.2.3)$$

According to Eq. (1.2.3), the characteristics of particle nature (i.e. mass  $m$ ) and wave nature (i.e. wavelength  $\lambda$ ) are inversely related to each other. Now  $c$  in Eq. (1.2.3) is the velocity of the photon, and thus  $mc$  may be considered to be the momentum  $p$  of the light photon. Thus, we have

$$p = \frac{h}{\lambda} \quad (1.2.4)^{\dagger}$$

For ordinary material particles, de Broglie suggested that  $c$  may be considered to be equivalent to  $v$  (i.e. their velocities) and thus Eq. (1.2.4) is also applicable to the material particles.

If the mass of a particle is small, as in the case of subatomic particles, the wavelength is significant, i.e. for them wave nature is expected. For a particle of larger mass, the wavelength is too small to be of any practical significance.

As an example, let us calculate the wavelength  $\lambda$  for an electron accelerated through a certain potential difference  $V$ . The kinetic energy of the electron would be given by the relation

$$\frac{1}{2} mv^2 = eV$$

and thus its momentum is

$$p = mv = m \left( \frac{2eV}{m} \right)^{1/2} = (2meV)^{1/2} \quad (1.2.5)$$

Substituting Eq. (1.2.5) in Eq. (1.2.4), we have

$$\lambda = \frac{h}{p} = \frac{h}{(2meV)^{1/2}} = \frac{h}{(2me)^{1/2}} V^{-1/2}$$

Substituting the values, of  $h$ ,  $m$  and  $e$ , we have

$$\lambda = \frac{6.626 \times 10^{-34} \text{ J s}}{\{2(9.109 \times 10^{-31} \text{ kg})(1.602 \times 10^{-19} \text{ C})\}^{1/2}} V^{-1/2} \quad (1.2.6)$$

$\lambda/m = 1.227 \times 10^{-9} \text{ (V/volt)}^{-1/2}$

For example, for the potential difference of 300 volt, we have

<sup>†</sup> See Annexure I at the end of the chapter for the derivation of Eq. (1.2.4) based on Einstein's theory of relativity.

### Experimental Verification of Wave Nature of Electron

The appearance of phenomena of diffraction and interference depends on one important factor that the dimensions of the object with which the wave strikes should be of the order of the wavelength of the wave. For ordinary light, one can use diffraction gratings having approximately 4000 lines/cm. However, for electrons, if we want to test its wave nature, we have to use a diffraction grating which should have approximately  $10^8$  lines/cm.

The first experimental demonstration of the wave nature of electron was provided by Clinton Davisson and Lester Germer. They used a thin nickel crystal as the target element. The spacing between the regularly spaced atoms in nickel crystal are of the order of the wavelength of the electron. From the diffraction pattern, Davisson and Germer also calculated the wavelength of the electron which agrees with the value obtained from the de Broglie's equation.

Later on, the wave nature of other material particles such as proton, neutron, hydrogen atom, and  $\alpha$ -particles have been demonstrated and the results of these experiments have shown that the de Broglie relation is generally applicable and that all particles behave in a wave-like manner under appropriate experimental conditions.

### Comment on the Wave Nature of Particles of Larger Masses

Lastly, a word about the wave nature of particles of larger masses such as baseballs, dust particles, etc., may be made. According to the de Broglie relation, such types of particles ought to have an associated wavelength though its value may be very small. Now, in order to detect these waves, we will have to have a target material whose dimensions is of the same order as that of the wavelength of the wave. For any macroscopic particle, even for a dust mote, the momentum is so great as to indicate a wavelength much shorter than the dimensions of any physical object; so these wave properties can never be observed.

### Application of the de Broglie Relation to the Hydrogen Atom

$$2\pi r = n\lambda \quad ; \quad \text{where } n = 1, 2, \dots \quad (1.2.7)$$

If the above condition is not satisfied, the positions of the maxima would change each time the electron went around the nucleus and thus the wave would not be stationary (Fig. 1.2.1).

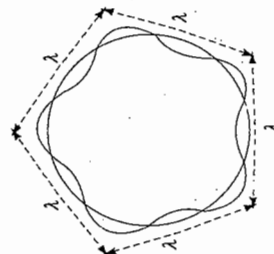


Fig. 1.2.1 A standing electron wave in the Bohr's orbit

Introducing de Broglie's relation in Eq. (1.2.7), we have

$$2\pi r = n \left( \frac{h}{p} \right) \quad \text{or} \quad pr = L = n \left( \frac{h}{2\pi} \right) \quad (1.2.8)$$

a relation which was introduced by Bohr while describing his theory of atomic structure.

### Example 1.2.1

#### Solution

What is the speed and de Broglie wavelength of an electron that has been accelerated by a potential difference of 500 V?

Since  $\frac{1}{2} mv^2 = eV$ , we have

$$v = \left( \frac{2eV}{m} \right)^{1/2} = \left\{ \frac{2(1.602 \times 10^{-19} \text{ C})(500 \text{ V})}{9.109 \times 10^{-31} \text{ kg}} \right\}^{1/2} = 1.326 \times 10^7 \text{ m s}^{-1}$$

$$\text{Now } \lambda = \frac{h}{(2meV)^{1/2}} = \frac{(6.626 \times 10^{-34} \text{ J s})}{\left\{ 2(9.109 \times 10^{-31} \text{ kg})(1.602 \times 10^{-19} \text{ C})(500 \text{ V}) \right\}^{1/2}}$$

$$= 0.55 \times 10^{-10} \text{ m}$$

### Example 1.2.2

#### Solution

(a) What is the speed of an electron whose de Broglie wavelength is 0.1 nm? (b) What potential difference must have such an electron been accelerated from an initial speed of zero? (c) If all of the energy of such an electron be transferred to a single photo what is the wavelength of this photon?

(a) From de Broglie relation, we have

$$v = \frac{h}{m\lambda}$$

Substituting the given values, we have

$$v = \frac{(6.626 \times 10^{-34} \text{ J s})}{(9.109 \times 10^{-31} \text{ kg})(0.1 \times 10^{-9} \text{ m})} = 7.274 \times 10^6 \text{ m s}^{-1}$$

(b) From Eq. (1.2.6), we have

$$\lambda/m = 1.227 \times 10^{-9} \text{ (V/volt)}^{-1/2}$$

$$\text{V/volt} = \left( \frac{1.227 \times 10^{-9}}{\lambda/m} \right)^2 = \left( \frac{1.227 \times 10^{-9}}{0.1 \times 10^{-9}} \right)^2 = 150.6$$

(c) The kinetic energy of the electron

$$\begin{aligned} &= \frac{1}{2} mv^2 = \frac{1}{2} (9.109 \times 10^{-31} \text{ kg}) (7.274 \times 10^6 \text{ m s}^{-1})^2 \\ &= 2.414 \times 10^{-17} \text{ J} \end{aligned}$$

Equating this to the energy of photon, we get

$$\frac{hc}{\lambda} = 2.414 \times 10^{-17} \text{ J}$$

$$\begin{aligned}\text{or } \lambda &= \frac{hc}{2.414 \times 10^{-17} \text{ J}} = \frac{(6.626 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m s}^{-1})}{(2.414 \times 10^{-17} \text{ J})} \\ &= 8.24 \times 10^{-9} \text{ m}\end{aligned}$$

### THE UNCERTAINTY PRINCIPLE

In de Broglie's relation, the particle nature of the matter is characterized by the term momentum  $p$  and the wave nature by the term wavelength  $\lambda$ . The two terms are inversely related to each other. In other words, we can say that the particle nature is inversely related to the wave nature, i.e. if  $p$  is larger,  $\lambda$  has a smaller value and vice versa. For a macroscopic particle which has a larger value of  $p$ , the wavelength as calculated from the de Broglie's relation is too small to be determined experimentally. For such a case, the wave nature may be completely ignored and thus the particle has only the corpuscular nature. The motion of such a particle is governed by the classical Newton's law of motion. At any instant, the precise value of its position can be calculated from the Newton's law and can also be determined experimentally. Thus, the motion of the particle can be described by a well-defined trajectory. However, the same is not true for a subatomic particle such as electron, proton, etc., which besides the particle nature also have the significant wave nature. The question that whether the position and the momentum of subatomic particles can be determined simultaneously with great accuracy was answered on the theoretical reasoning by Heisenberg. According to him, *it is not possible to design an experiment with the help of which one can determine simultaneously the precise values of both the position and the momentum of subatomic particles.*

To understand the principle, we consider the following example.

Consider an electron whose position is to be determined with the help of a microscope. For this, we will employ a light whose photon on striking with the electron should come within the preview of the microscope, i.e. within the cone of angle  $2\alpha$  as shown in Fig. 1.2.2.

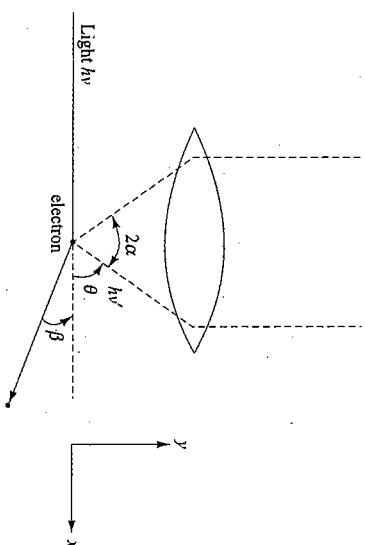


Fig. 1.2.2 Location of the electron with the help of a microscope

The frequency of the scattered photon will undergo a Compton shift. The electron on striking the photon will acquire a momentum and will move in a direction making an angle  $\beta$  with the  $x$ -axis as shown in Fig. 1.2.2. The momentum of the photon before and after the collision can be calculated from the de Broglie's relation. Thus, we have

Momentum of the photon before the collision,

$$p_1 = \frac{h}{\lambda} = \frac{h\nu}{c}$$

Momentum of the photon after the collision,

$$p_2 = \frac{h}{\lambda'} = \frac{h\nu'}{c}$$

Now, by the law of conservation of energy, we have

$$h\nu = h\nu' + \frac{1}{2} m v^2 = h\nu' + \frac{p^2}{2m} \quad (1.2.9)$$

and the corresponding expressions for the conservation of momentum in the  $x$  and  $y$ -directions are

$$\text{For } x\text{-component: } \frac{h\nu}{c} = \frac{h\nu'}{c} \cos \theta + p \cos \beta \quad (1.2.10)$$

$$\text{For } y\text{-component: } 0 = \frac{h\nu'}{c} \sin \theta - p \sin \beta \quad (1.2.11)$$

Eliminating  $\beta$  from Eqs (1.2.10) and (1.2.11), we have

$$\frac{h\nu}{c} = \frac{h\nu'}{c} \cos \theta + p \sqrt{1 - \left( \frac{h\nu'}{pc} \sin \theta \right)^2}$$

Substituting the value of  $h\nu'$  from Eq. (1.2.9), we have

$$\frac{h\nu}{c} = \frac{1}{c} \left( h\nu - \frac{p^2}{2m} \right) \cos \theta + p \sqrt{1 + \left( \frac{h\nu - p^2/2m}{pc} \sin \theta \right)^2} \quad (1.2.12)$$

Equation (1.2.12) relates the momentum which the electron acquires and the angle  $\theta$  to which the incident radiation is deflected. Now the electron will be detected if the scattered photon passes through the aperture of the microscope, i.e. within the cone of angle  $2\alpha$  as shown in Fig. 1.2.2. Thus, the angle  $\theta$  to which the electron deviates may have any value between  $90^\circ \pm \alpha$  in order that it passes through the indicated cone. Thus, we have a range  $\Delta\theta$  from  $(90 - \alpha)$  to  $(90 + \alpha)$ . Consequently, the momentum of the scattered photon will have a range of values. We may call the uncertainty in the value of the momentum. Thus, localizing the electron introduces some uncertainty in its momentum value and therefore a precise value cannot be determined.

An approximate expression connecting the uncertainty in the value of  $x$  corresponding uncertainty in the value of  $p$  can be derived starting from Eq. (1.2.12).

### Approximate Expression of Uncertainty Principle



We have

$$\frac{h\nu}{c} = \frac{h\nu'}{c} \cos \theta + p \cos \beta$$

$$\text{or} \quad p \cos \beta = \frac{h\nu}{c} - \frac{h\nu'}{c} \cos \theta \simeq \frac{h\nu}{c} (1 - \cos \theta) \quad (1.2.13)$$

The left side of Eq. (1.2.13) represents the component of momentum of the electron along the  $x$ -axis. Since the electron will be detected for any value of the angle between  $90^\circ \pm \alpha$ , the momentum of electron may have any value between the two extremes given below.

$$\frac{h\nu}{c} [1 - \cos (90^\circ - \alpha)] = \frac{h\nu}{c} (1 - \sin \alpha)$$

$$\text{and} \quad \frac{h\nu}{c} [1 - \cos (90^\circ + \alpha)] = \frac{h\nu}{c} (1 + \sin \alpha)$$

Thus, the uncertainty in the value of  $p$  is

$$|\Delta p| = \frac{2h\nu}{c} \sin \alpha \quad (1.2.14)$$

Now the accuracy with which an object can be located through a microscope depends upon the wavelength of the radiation employed and according to the principles of optics, it is given as

$$\Delta x \simeq \frac{\lambda}{\sin \alpha} = \frac{c}{\nu \sin \alpha} \quad (1.2.15)$$

Thus, we have

$$\Delta p \Delta x = \left( \frac{2h\nu}{c} \sin \alpha \right) \left( \frac{c}{\nu \sin \alpha} \right) \simeq 2h \quad (1.2.16)^\dagger$$

Equations (1.2.14) and (1.2.15) may be interpreted as follows. According to Eq. (1.2.14), the uncertainty in the value of the momentum will depend upon the angle  $\alpha$ . Thus, by making  $\alpha$  small (i.e. by using a microscope of smaller aperture)

<sup>†</sup> The exact expression of uncertainty principle as given by Heisenberg is

$$\Delta p \Delta x \geq \frac{h}{4\pi} \quad (1.2.17)$$

where  $\Delta p$  and  $\Delta x$  are the root mean square uncertainties in momentum and position, respectively. These are defined as follows.

$$\Delta p = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2} \quad \text{and} \quad \Delta x = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2} \quad (1.2.18)$$

where the symbol  $\langle \rangle$  represents an average value (see Section 1.3, Eq. 1.3.13 for evaluating the average value).

The variables position and momentum constitute what is called a conjugate pair of variables. Equation (1.2.17) is applicable for any conjugate pair of variables. Energy and time is one of the examples, for which we have

$$\Delta E \Delta t \geq \frac{h}{4\pi}$$

### Consequences of Uncertainty Principle

the value of  $\Delta p$  can be made smaller (or the value of  $p$  becomes more precise). But once we make  $\alpha$  smaller, according to Eq. (1.2.15), this will increase the corresponding uncertainty in  $x$  (i.e. the position of the object becomes less precise). On the other side, if we employ a radiation of high frequency such as  $\gamma$  radiation, though it decreases the uncertainty in  $x$  yet it makes the corresponding uncertainty in  $p$  larger. Thus, it may be concluded that the precise values of both  $x$  and  $p$  cannot be determined simultaneously, only one of them can be determined precisely at the cost of the other. The fundamental cause of the uncertainty principle lies in the fact that the particle under observation interacts with the measuring system. In the determination of the position of an object as seen above, a beam of light is directed on the object and thus the latter suffers a recoil which alters its momentum.

One of the direct consequences of the uncertainty principle is that the subatomic particles such as electrons, protons, etc., cannot have well-defined trajectories, since for such particles both the position and the velocity (or momentum) cannot have precise values. Take, for example, the case of an electron in the atom. Let us say that the position of the electron from the nucleus can be determined with an uncertainty of 5 pm. Say, for instance, the electron in the first Bohr orbit lies between the  $r$  values of 50.4 pm and 55.4 pm. The corresponding minimum uncertainty in  $v$  can be calculated by using the uncertainty principle. Thus, we have

$$\Delta x \Delta p = (\Delta x) (m \Delta v) = \frac{h}{4\pi}$$

$$\text{or} \quad \Delta v = \frac{h}{4\pi m \Delta x}$$

Substituting the values, we get

$$\Delta v = \frac{(6.626 \times 10^{-34} \text{ J s})}{4(3.14)(9.109 \times 10^{-31} \text{ kg})(5 \times 10^{-12} \text{ m})} = 1.158 \times 10^7 \text{ m s}^{-1}$$

If the velocity of the electron becomes uncertain by this huge amount (which is, in fact, comparable with the velocity which the electron is expected to possess from Bohr's theory), then there is hardly any point in talking about its precise velocity. Consequently, its trajectory cannot be defined. In this respect, the Bohr model is a complete failure since it assumes the existence of well-defined orbits in which both the position and the momentum of the electron are known exactly.

The uncertainty principle has a negligible effect on the uncertainty of position (or momentum) for macroscopic particles. Take, for example, a cricket ball whose mass is 200 g. If the uncertainty in its position is again of the order of 5 pm then the corresponding uncertainty in its velocity would be

$$\Delta v = \frac{h}{4\pi m \Delta x} = \frac{(6.626 \times 10^{-34} \text{ J s})}{4(3.14)(0.200 \text{ kg})(5 \times 10^{-12} \text{ m})} = 5.28 \times 10^{-23} \text{ m s}^{-1}$$

This uncertainty is definitely negligible in comparison to the usual velocity of the cricket ball and thus it will have precise values of position and velocity and

hence a precise trajectory. For macroscopic particles, classical mechanics may be employed without any detectable discrepancies.

### 1.3 SCHRÖDINGER WAVE THEORY

#### Necessity of Wave Theory

Bohr's theory is based on the corpuscular nature of electron. We have seen that this theory, besides being inadequate, also violates the two fundamental laws governing the behaviour of the electron, viz., de Broglie's relation and the uncertainty principle. Hence, this theory has to be replaced by a more complete theory which takes into account the wave-particle duality and the probable distribution of the electron instead of the well-defined trajectory. In 1926, Schrödinger proposed the wave theory which is essentially based on the assumption that the behaviour of an electron in an atom can be described by an equation analogous to that used to describe the standing wave systems such as the vibrating string fixed at both the ends. An alternative theory was developed by Heisenberg and is known as matrix mechanics. Schrödinger later showed that the two mechanics, namely, wave and matrix, are essentially the same. Of these two mechanics, the wave mechanics have proved to be more useful in applications to chemistry.

The equation used for the wave motion in one direction is

$$\left( \frac{\partial^2 \psi}{\partial x^2} \right)_t = \frac{1}{u^2} \left( \frac{\partial^2 \psi}{\partial t^2} \right)_x \quad (1.3.1)$$

where  $\psi$  is the amplitude of vibration at any point whose coordinate is  $x$  at a time  $t$ , and  $u$  is the speed of propagation of the wave. If  $u$  does not depend on the time, the displacement  $\psi$  can be written as a product of two functions, one depending only on the space coordinates  $x$  and the other depending periodically on the time. Thus the form of  $\psi$  is

$$\psi = \psi(x) \exp\{i(2\pi\nu t)\} \quad (1.3.2)$$

where  $\nu$  is the frequency of the wave and  $i = \sqrt{-1}$ . Substituting Eq. (1.3.2) in Eq. (1.3.1), we get

$$\left( \frac{\partial^2 \psi \exp\{i(2\pi\nu t)\}}{\partial x^2} \right)_t = \frac{1}{u^2} \left( \frac{\partial^2 \psi \exp\{i(2\pi\nu t)\}}{\partial t^2} \right)_x$$

$$\text{or} \quad \exp\{i(2\pi\nu t)\} \frac{d^2 \psi}{dx^2} = \frac{1}{u^2} \psi (2\pi\nu)^2 \exp\{i(2\pi\nu t)\}$$

$$\text{or} \quad \frac{d^2 \psi}{dx^2} = -\frac{4\pi^2 \nu^2}{u^2} \psi \quad (1.3.3)$$

The frequency  $\nu$  of the vibration and the speed  $u$  are related by the equation

$$u = \lambda \nu \quad (1.3.4)$$

where  $\lambda$  is the wavelength of the associated wave. Substituting Eq. (1.3.4) in Eq. (1.3.3), we get

$$\frac{d^2 \psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad (1.3.5)$$

#### Eigenvalue Problem

Equation (1.3.5) does not include the time variable  $\exp\{i(2\pi\nu t)\}$  and thus gives only the vibration of the amplitude function with  $x$ . Equation (1.3.5) may be interpreted as follows. The term  $d^2/dx^2$  is an operator which on operating on the function  $\psi$  gives back the function  $\psi$  multiplied by a constant  $-4\pi^2/\lambda^2$ . The equation of this type is known as the *eigenvalue equation*, the function  $\psi$  is an *eigenfunction* and the constant  $(-4\pi^2/\lambda^2)$ , in this case, is an *eigenvalue* (sometimes it is referred to as the proper value or characteristic value). In order that the function  $\psi$  is an acceptable solution of Eq. (1.3.5), it has to be consistent with the basic constraints. In the case of a vibrating string (Fig. 1.3.1) these are:

- The function  $\psi$  must be zero at each end of the string, since the system is fixed at these points and thus amplitudes are zero.
- The  $\psi$  must be a *single valued* and *finite* between the limits of  $x$  varying from one end to the other.

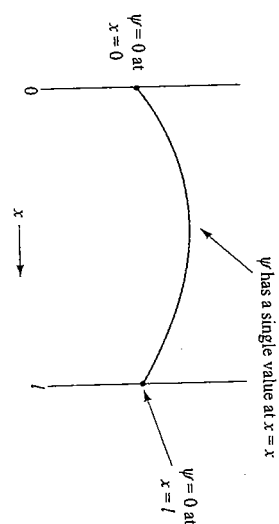


Fig. 1.3.1 Vibrating string fixed at both ends

Equation (1.3.5) can be extended to describe motion in three dimensions by replacing  $\psi(x)$  by  $\psi(x, y, z)$  and the operator  $d^2/dx^2$  by

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Thus, we have

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad (1.3.6)$$

Equation (1.3.6) may be written in a more concise form as

$$\nabla^2 \psi + \frac{4\pi^2}{\lambda^2} \psi = 0 \quad (1.3.7)$$

where  $\nabla^2$  is written for  $(\partial^2/\partial x^2) + (\partial^2/\partial y^2) + (\partial^2/\partial z^2)$  and is known as *Laplacian operator*. It is pronounced as *del squared*.

According to Schrödinger, Eq. (1.3.7) can also be applied to all subatomic particles (electrons, protons, etc.) in an atom. In order that this equation also takes care of wave-particle duality, Schrödinger replaced  $\lambda$  in terms of momentum by employing the de Broglie's relation,  $\lambda = h/p$ . With this Eq. (1.3.7) becomes

$$\nabla^2 \psi + \frac{4\pi^2 p^2}{h^2} \psi = 0 \quad (1.3.8)$$

#### Equation Representing Standing Wave System

For an electron in an atom, the total energy of the electron is the sum of its kinetic and potential energies, i.e.

$$E = KE + PE = (1/2)mv^2 + V$$

$$\text{or } E = \frac{p^2}{2m} + V$$

$$\text{or } p^2 = 2m(E - V) \quad (1.3.9)$$

Substituting Eq. (1.3.9) in Eq. (1.3.8), we have

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad (1.3.10)$$

Equation (1.3.10) is the Schrödinger equation which describes the behaviour of electron in an atom.

The Schrödinger wave equation (1.3.10) can be obtained from certain postulates without referring to the propagation of waves. These are:

- For every state of a time independent physical system, a function  $\psi$  of the coordinates can be written. Knowledge of this function permits a complete description of the state of system.
- The function  $\psi$  must be a single valued, continuous and finite throughout the configuration space. It must be quadratically integrable. Besides this, if the problem under study does not involve any discontinuity at the boundary, the first derivative of the function  $\psi$  must also be continuous.
- Corresponding to every observable quantity in classical mechanics, e.g. position, momentum or energy, there corresponds a linear mathematical operator.<sup>†</sup> The form of the operator can be obtained from the classical expressions for the observables according to definite rules. These are:

- (a) The operation corresponding to the position coordinate is multiplication by the value of that coordinate, i.e.  $x \rightarrow x$ .

- (b) The operation representing the components of momentum are:

$$p_x = \frac{h}{2\pi i} \frac{\partial}{\partial x}; \quad p_y = \frac{h}{2\pi i} \frac{\partial}{\partial y}; \quad p_z = \frac{h}{2\pi i} \frac{\partial}{\partial z} \quad (1.3.11)^\dagger$$

<sup>†</sup> By definition, an operator is a description of a mathematical operation that is to be carried out on a function to obtain a new function. Some common examples are multiplication by a number or a constant, square root,  $d/dx$  and  $d^2/dx^2$ . An operator is said to be linear if it satisfies the relation

$$\alpha_{op}(C\psi) = C(\alpha_{op}\psi)$$

where  $C$  is a constant. For example, the operator  $d/dx$  is a linear operator. An operator which takes the square root of a function is a nonlinear operator since  $\sqrt{(C\psi)} \neq C(\sqrt{\psi})$ . All the quantum mechanical operators are linear.

<sup>‡</sup> The form of operators given by Eq. (1.3.11) may be taken as such without any rigorous derivation. However, these can be derived by combining the wave expression (Eq. 1.3.5) with de Broglie relation as shown in the following.

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi = -\frac{4\pi^2}{(h/p_x)^2} \psi = \left(\frac{2\pi i}{h}\right)^2 p_x^2 \psi$$

$$\text{or } \left(\frac{h}{2\pi i} \frac{d}{dx}\right)^2 \psi = p_x^2 \psi \quad \text{or } \frac{h}{2\pi i} \frac{d}{dx} \psi = p_x \psi$$

From this equation, it follows that  $(h/2\pi i) (\partial/\partial x)$  is the operator for the  $x$ -component of momentum.

- For a given operator  $A_{op}$ , (also represented as  $\hat{A}$ ) it is possible to write  $A_{op}\psi = a\psi$  (1.3.12)

This means that when the operator  $A_{op}$  acts on the function  $\psi$ , which is supposed to be suitable for this operator, gives back the function  $\psi$  multiplied by a constant quantity  $a$ . For the given state, known as the eigenstate of the system,  $\psi$  is the eigenfunction for the operator  $A_{op}$  and  $a$  is the corresponding eigenvalue.

- The expectation value of the operator  $A_{op}$  is a statistical average of the observed values of the quantity for which the operator  $A_{op}$  stands for. This expectation value,  $\langle A \rangle$ , is related to the wave function of the system by

$$\langle A \rangle = \frac{\int \psi^* A_{op} \psi d\tau}{\int \psi^* \psi d\tau} \quad (1.3.13)$$

where the integration extends over the whole of configuration space. By using Eq. (1.3.12) it can be shown that for an eigenfunction the expectation value of  $A_{op}$  is equal to the eigenvalue  $a$ :

$$\langle A \rangle = \frac{\int \psi^* A_{op} \psi d\tau}{\int \psi^* \psi d\tau} = \frac{\int \psi^* (a\psi) d\tau}{\int \psi^* \psi d\tau} = a \frac{\int \psi^* \psi d\tau}{\int \psi^* \psi d\tau} = a$$

The expectation value  $\langle A \rangle$  evaluated from the well-behaved approximate wave function is always found to be greater than the true eigenvalue. This is, in fact, the statement of *variation theorem* (see Section 1.11).

With the postulates listed above, it is possible to derive the Schrödinger equation in a very simple manner.

Consider an electron in an atom. Its total energy  $E$  is given by

$$E = T + V = \frac{1}{2} mv^2 + V = \frac{p^2}{2m} + V$$

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V \quad (1.3.14)$$

This classical expression of the quantity  $E$  can be converted to the corresponding quantum mechanical operator for energy by the following replacements.

$$p_x \rightarrow \frac{h}{2\pi i} \frac{\partial}{\partial x}; \quad p_y \rightarrow \frac{h}{2\pi i} \frac{\partial}{\partial y}; \quad p_z \rightarrow \frac{h}{2\pi i} \frac{\partial}{\partial z}$$

$$\text{and } V \rightarrow V$$

The operator corresponding to the energy  $E$  is called the *Hamiltonian operator* and is represented by the symbol  $H_{op}$ . Thus, we have

$$H_{op} = \frac{1}{2m} \left\{ \left( \frac{h}{2\pi i} \frac{\partial}{\partial x} \right)^2 + \left( \frac{h}{2\pi i} \frac{\partial}{\partial y} \right)^2 + \left( \frac{h}{2\pi i} \frac{\partial}{\partial z} \right)^2 \right\} + V$$

$$= -\frac{h^2}{8\pi^2 m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V \quad (1.3.15)$$

$$\text{or} \quad H_{op} = -\frac{h^2}{8\pi^2 m} \nabla^2 + V \quad (1.3.16)$$

Now according to Eq. (1.3.12), we have

$$H_{op} \psi = E \psi \quad (1.3.17)$$

where  $E$  is the eigenvalue of the Hamiltonian operator  $H_{op}$ , a quantity which has a precise value for a given state. Thus

$$\left( -\frac{h^2}{8\pi^2 m} \nabla^2 + V \right) \psi = E \psi$$

$$\text{or} \quad \nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad (1.3.18)$$

which is the required Schrödinger equation.

### Born Interpretation of the Wave Function

As stated earlier, a complete description of the state of the system can be described by its state function  $\psi$ . In Eq. (1.3.2), the function  $\psi$  represents the amplitude of vibration at any point. In the classical theory of electromagnetic radiation, the square of the amplitude is proportional to the intensity of the light. A very similar concept was suggested by Born in quantum mechanics according to which *the square of the function  $\psi$  at any point is proportional to the probability density of finding the system at the point*. This definition of probability is in agreement with the uncertainty principle as one cannot talk about the precise position of a subatomic particle. Now the function  $\psi$  may be real or imaginary. Since the probability of finding a material particle at a given point in space has to be real, the term  $\psi^2$  has to be replaced by  $\psi^* \psi$ , where  $\psi^*$  is the complex conjugate of  $\psi$ . The complex conjugate can be obtained by replacing  $i$  ( $=\sqrt{-1}$ ) by  $-i$ .

The probability of finding the particular system in the small volume element  $dxdydz$  situated at a point in space is proportional to

$$\psi^* \psi dxdydz \quad \text{or} \quad \psi^* \psi d\tau \quad (1.3.19)$$

where  $d\tau = dxdydz$  and it represents the small element of the configuration space (the whole of the space where the system may occur) of the system.

### Normalized Wave Function

Integration of Eq. (1.3.19) over the whole of the configuration space gives a quantity which is proportional to the total probability of the system. It is obvious that this total probability will be equal to unity. Generally, we may have

$$\int \psi^* \psi d\tau = N$$

where  $N$  is a constant. If this integration over the whole of the configuration space is to be made equal to the total probability (i.e. unity), obviously we must have

$$\frac{1}{N} \int \psi^* \psi d\tau = 1 \quad \text{or} \quad \int \left( \frac{1}{N^{1/2}} \psi^* \right) \left( \frac{1}{N^{1/2}} \psi \right) d\tau = 1 \quad (1.3.20)$$

The factor  $1/N^{1/2}$  is known as the *normalization constant* which is independent of the coordinates  $x$ ,  $y$  and  $z$ . The function  $(1/N^{1/2})\psi$  is known as the *normalized function*. The latter like the unnormalized function also satisfies the wave equation.

The solution of Schrödinger equation quite often provides more than one wave function, i.e. each wave function satisfies the Schrödinger equation with its own characteristic eigenvalue. If two such wavefunctions satisfy the expression

$$\int \psi_i \psi_j d\tau = 0$$

then the two functions are said to be orthogonal to each other. The two wave functions are the independent solutions of the same Schrödinger equation.

If the solutions of Schrödinger equation satisfy the expression

$$\int \psi_i \psi_j d\tau = \delta_{ij} \quad \begin{cases} \delta_{ij} = 0 & \text{if } i \neq j \\ \delta_{ij} = 1 & \text{if } i = j \end{cases}$$

then the solutions form orthonormal set of wave functions. The symbol  $\delta_{ij}$  is called the Kronecker delta.

#### Problem 1.3.1

The operator  $A_{op}$  is said to be a Hermitian operator if it satisfies the expression

$$\int \psi_n^* A_{op} \psi_m d\tau = \int \psi_m^* A_{op} \psi_n d\tau$$

where  $\psi_n$  and  $\psi_m$  are the two eigenfunctions of  $A_{op}$ . Prove that (a) the eigenvalues of a Hermitian operator are all real, and (b) the nondegenerate eigenfunctions of a Hermitian operator are orthogonal to each other, i.e. the expression  $\langle \psi_n | \psi_m \rangle = 0$  holds good.

(a) Let  $\psi_n$  be one of the eigenfunctions of the operator  $A_{op}$  and let  $\alpha_n$  be the corresponding eigenvalue. We will have

$$A_{op} \psi_n = \alpha_n \psi_n \quad (1)$$

Multiplying both sides of Eq. (1) by  $\psi_n^*$  and then integrating, we get

$$\int \psi_n^* A_{op} \psi_n d\tau = \alpha_n \int \psi_n^* \psi_n d\tau \quad (2)$$

The complex conjugate of Eq. (2) must also be valid. Thus, we have

$$\int \psi_n^* A_{op}^* \psi_n^* d\tau = \alpha_n^* \int \psi_n^* \psi_n^* d\tau \quad (3)$$

Since  $A_{op}$  is Hermitian, the left sides of Eqs (2) and (3) are equal. Thus, we have

$$\alpha_n \int \psi_n^* \psi_n d\tau = \alpha_n^* \int \psi_n \psi_n^* d\tau \text{ or } (\alpha_n - \alpha_n^*) \int \psi_n^* \psi_n d\tau = 0 \quad (4)$$

Since  $\int \psi_n^* \psi_n d\tau$  is nonzero, we must have

$$\alpha_n = \alpha_n^* \quad (5)$$

which will be applicable only when the eigenvalue  $\alpha$  is real.

(b) Let  $\alpha_m$  and  $\alpha_n$  be the eigenvalues of the functions  $\psi_m$  and  $\psi_n$ , respectively. We will have

$$A_{op} \psi_m = \alpha_m \psi_m \quad (6)$$

$$A_{op}^* \psi_n^* = \alpha_n^* \psi_n^* \quad (7)$$

Multiplying Eq. (6) by  $\psi_n^*$  and integrating, we get

$$\int \psi_n^* A_{op} \psi_m d\tau = \alpha_m \int \psi_n^* \psi_m d\tau \quad (8)$$

Similarly, multiplying Eq. (7) by  $\psi_m$  and integrating, we get

$$\int \psi_m A_{op}^* \psi_n^* d\tau = \alpha_n^* \int \psi_n^* \psi_m d\tau \quad (9)$$

Since  $A_{op}$  is Hermitian, the left sides of Eqs (8) and (9) are equal. Thus, we have

$$\alpha_m \int \psi_n^* \psi_m d\tau = \alpha_n^* \int \psi_n^* \psi_m d\tau$$

$$\text{or } (\alpha_m - \alpha_n^*) \int \psi_n^* \psi_m d\tau = 0$$

Since  $\alpha_m$  are the two different eigenvalues, we must have

$$\int \psi_n^* \psi_m d\tau = 0 \quad (10)$$

### Problem 1.3.2

The well-behaved approximate wave function  $\psi$  of an operator  $A_{op}$  can be expressed in terms of its orthonormal set of eigenfunctions  $\phi_i$  by the expression

$$\psi = \sum_i c_i \phi_i$$

This expansion is known as a Fourier expansion or a Fourier series. The coefficients  $c_i$  are called Fourier coefficients. Show that the expectation value  $\langle A \rangle$  for the function  $\psi$  is the statistical average of the true eigenvalues of the operator  $A_{op}$ .  
The expectation value  $\langle A \rangle$  for the function  $\psi$  is defined as

$$\langle A \rangle = \frac{\int \psi A_{op} \psi d\tau}{\int \psi \psi d\tau}$$

Replacing  $\psi = \sum_i c_i \phi_i$ , we get

$$\begin{aligned} \langle A \rangle &= \frac{\int \{(\sum_i c_i \phi_i) A_{op} (\sum_i c_i \phi_i)\} d\tau}{\int (\sum_i c_i \phi_i)^2 d\tau} \\ &= \frac{\int \{(\sum_i c_i \phi_i) (\sum_i c_i A_{op} \phi_i)\} d\tau}{\int (\sum_i c_i \phi_i)^2 d\tau} = \frac{\int \{(\sum_i c_i \phi_i) (\sum_i c_i a_i \phi_i)\} d\tau}{\int (\sum_i c_i \phi_i)^2 d\tau} \end{aligned}$$

Using the fact that  $\int \phi_i \phi_j d\tau = \delta_{ij}$ , we will get

$$\langle A \rangle = \frac{\sum_i c_i^2 a_i}{\sum_i c_i^2}$$

If the function  $\psi$  is a normalized wave function, then  $\sum_i c_i^2 = 1$ . The quantity measures the probability of observing the eigenvalue  $a_i$ . Hence

$$\langle A \rangle = \sum_i c_i^2 a_i = \text{statistical average of the eigenvalues } a_i$$

## 1.4 QUANTIZATION OF TRANSLATIONAL ENERGY

### Introduction

A molecule may have three types of motions, viz., translational, rotational and vibrational. According to classical mechanics, the energy associated with each of the three motions can vary continuously, i.e. it can have any value. But, according to wave mechanics, these energies are quantized, i.e. they vary in a discontinuous manner. We now consider the translational motion from the wave-mechanical viewpoint and show, taking a typical example of a particle in a box, how and why the quantization of energy takes place.

### PARTICLE IN A ONE-DIMENSIONAL BOX

For the sake of simplicity, we start with the motion of a particle in a one-dimensional box and then treat the motion in a three-dimensional box. Let a particle of mass  $m$  be moving in a one-dimensional box of length  $l$  without experiencing any potential energy, i.e.  $V = 0$ . The particle is not allowed to move outside this box. This can be achieved by setting a very high potential energy of infinity at the sides of the box, so that the moment the particle reaches the wall, it is reflected back instead of penetrating or crossing of the wall (Fig. 1.4.1).

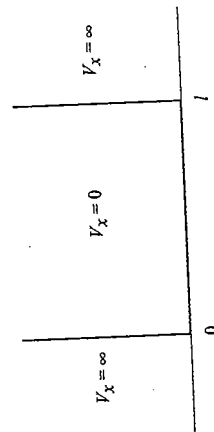


Fig. 1.4.1 The particle in a box with  $V_x = 0$  within the box and  $V_x = \infty$  outside the box

**Wave Function of the Particle Outside the Box**

Starting with the one-dimensional Schrödinger equation, we have

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E - V)\psi = 0 \quad (1.4.1)$$

The function  $\psi$  will depend only on one independent variable, viz.,  $x$ -coordinate. Outside the box, Eq. (1.4.1) takes the form

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E - \infty)\psi = 0$$

Neglecting  $E$  in comparison to  $\infty$ , we have

$$\frac{d^2\psi}{dx^2} = \infty \times \psi \quad \text{or} \quad \psi = \frac{1}{\infty} \frac{d^2\psi}{dx^2}$$

that is,  $\psi = 0$  outside the box. This means that the particle cannot exist outside the region  $0 < x < l$ .

Within the box, the Schrödinger equation for the motion of the particle takes the form

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}E\psi = 0$$

$$\text{i.e.} \quad \frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \quad (1.4.2)$$

$$\text{where} \quad \alpha^2 = \frac{8\pi^2mE}{h^2} \quad (1.4.3)$$

A general solution of Eq. (1.4.2) is given by

$$\psi = A \sin(\alpha x) + B \cos(\alpha x) \quad (1.4.4)$$

where  $A$  and  $B$  are constants. From Eq. (1.4.4), a large number of wave functions differing in the values of  $A$ ,  $B$  and  $\alpha$  can be obtained. However, all such functions will not be acceptable for the motion of a particle in the box. Only those functions which satisfy the boundary conditions of  $\psi = 0$  at  $x = 0$  and  $x = l$  will be the acceptable wave functions.

For  $\psi = 0$  at  $x = 0$ , Eq. (1.4.4) becomes

$$0 = A \sin(\alpha \times 0) + B \cos(\alpha \times 0)$$

The above expression will be true only when  $B = 0$ . Thus, the wave function as given by Eq. (1.4.4) becomes

$$\psi = A \sin(\alpha x) \quad (1.4.5)$$

For  $\psi = 0$  at  $x = l$ , Eq. (1.4.5) becomes

$$0 = A \sin(\alpha l)$$

**Energies of the Particle**

The above expression will be true only when  $\alpha l$  is an integral multiple of  $\pi$ , i.e.,

$$\alpha l = n\pi \quad (1.4.6)$$

where  $n$  can have only integral values of 1, 2, 3, .... A value of  $n = 0$  is eliminated, since it leads to  $\alpha = 0$  or  $\psi(x) = 0$  everywhere within the box. Substituting  $\alpha$  from Eq. (1.4.6) in Eq. (1.4.5), we get

$$\psi = A \sin\left(\frac{n\pi}{l}x\right) \quad (1.4.7)$$

Now from Eq. (1.4.3), we have

$$\alpha^2 = \frac{8\pi^2mE}{h^2} \quad \text{or} \quad E = \frac{\alpha^2 h^2}{8\pi^2 m} \quad (1.4.8)$$

Substituting the value of  $\alpha$  from Eq. (1.4.6), we have

$$E = \frac{(n^2 \pi^2 / l^2) h^2}{8\pi^2 m}$$

$$\text{or} \quad E = n^2 \left( \frac{h^2}{8ml^2} \right) \quad (1.4.9)$$

Since the constant  $n$  can have only integral values, from Eq. (1.4.9) it follows that the energy associated with the motion of a particle in a box is quantized.

Thus in the present case,  $n$  represents the *quantum number*. The fact that the lowest value of energy which the particle can possess (zero point energy) is no zero is consistent with the uncertainty principle. According to the latter, if the particle is confined to within a finite region, it ought to have some kinetic energy.

The very important step which is responsible for introducing the quantization of energy may again be stressed here. According to Eq. (1.4.8),  $E$  can vary in continuous manner since  $\alpha$  can have any value. The function  $\psi = A \sin(\alpha x) + B \cos(\alpha x)$  with varying values of  $\alpha$  is still a solution of Schrödinger equation. But all these functions may not be the acceptable solutions for the system of particle in a box; only those functions which satisfy the boundary conditions of the system will be the acceptable solutions. The functions which are not consistent with the boundary conditions must be discarded along with the corresponding values of  $E$ . The rejected values of  $E$  will not be observed. Thus, the values of  $E$  are quantized. The moment we take into account the boundary conditions of  $\psi$  being zero at  $x = 0$  and  $x = l$ . It leads to the condition that  $\alpha$  cannot vary in a continuous manner but in a discrete manner and is given by

$$\alpha = n \left( \frac{\pi}{l} \right)$$

where  $n = 1, 2, 3, \dots$ . This finally leads to the quantization of energy which is given by

$$E = n^2 \left( \frac{h^2}{8ml^2} \right)$$

The difference between the two successive energy levels is

$$\Delta E = E_{n+1} - E_n = (2n+1)h^2/8ml^2 \quad (1.4.10)$$

The energy difference  $\Delta E$  decreases as the length of the box increases. The difference between the two levels becomes negligible when the box has a very large length. Thus, a free particle moving in an unbound region of space has unquantized translational energy levels. Even for a box of ordinary size,  $\Delta E$  is too small to be determined experimentally and hence atoms or molecules moving freely in such a box may be treated as though their translational energy is unquantized.

The second factor on which the value of  $\Delta E$  depends is the mass of the particle. The spacing between energy levels increases as the mass of the particle decreases. Thus, if a particle of very small mass such as the electron is confined to a very small box of the order of atomic diameters, we will have more widely-spaced energy levels. For particles of larger masses moving comparatively in a larger box, the energy separation will be too small to be determined experimentally and thus such systems will not show any quantum effects.

### Normalization of the Wave Function

The wave function as given by Eq. (1.4.7) contains the undetermined constant  $A$ . Its value can be determined through the total probability expression. Remembering that the particle remains within the box, it is obvious that its total probability of finding the particle from  $x = 0$  to  $x = l$  will be unity. Thus, we have

$$1 = \int_0^l \psi^* \psi dx = A^2 \int_0^l \sin^2 \left( \frac{n\pi}{l} x \right) dx = A^2 \int_0^l \left[ \frac{1 - \cos(2n\pi x/l)}{2} \right] dx$$

The value of the above integral is  $l/2$ , and thus, we have

$$1 = A^2 \frac{l}{2}, \quad \text{i.e.} \quad A = \sqrt{\frac{2}{l}}$$

Thus, the form of normalized wave function is

$$\psi = \sqrt{\frac{2}{l}} \sin \left( \frac{n\pi}{l} x \right) \quad (1.4.11)$$

**Orthogonality of the Wave Functions** From Eq. (1.4.11), a series of acceptable wave functions of particle in the one-dimensional box can be generated by assigning different permitted values of the quantum number  $n$ . Each eigenfunction is orthogonal to any other eigenfunction. By definition, the two functions are orthogonal if the integral

$$\int_{\text{all space}} \psi_m^* \psi_n d\tau = 0$$

where  $m$  and  $n$  are two different quantum numbers. For a particle in the one-dimensional box, we have

$$\psi_m^* = \psi_m = \sqrt{\frac{2}{l}} \sin \left( \frac{m\pi x}{l} \right)$$

$$\psi_n = \sqrt{\frac{2}{l}} \sin \left( \frac{n\pi x}{l} \right)$$

Thus, from the condition of orthogonality, we have

$$\int_0^l \psi_m^* \psi_n dx = \frac{2}{l} \int_0^l \sin \left( \frac{m\pi x}{l} \right) \sin \left( \frac{n\pi x}{l} \right) dx$$

Following the trigonometric equation

$$(\sin \alpha)(\sin \beta) = \frac{1}{2} \cos(\alpha - \beta) - \frac{1}{2} \cos(\alpha + \beta)$$

the above expression becomes

$$\frac{1}{l} \left[ \int_0^l \cos \left\{ (m-n)\pi \frac{x}{l} \right\} - \cos \left\{ (m+n)\pi \frac{x}{l} \right\} \right] dx$$

which on integration gives

$$\frac{1}{l} \left[ \frac{l}{(m-n)\pi} \sin \left\{ (m-n)\pi \frac{x}{l} \right\} - \frac{l}{(m+n)\pi} \sin \left\{ (m+n)\pi \frac{x}{l} \right\} \right]_0^l$$

Since  $m$  and  $n$  are integers, the above expression is numerically equal to zero.

The different wave functions generated by Eq. (1.4.11) are collective referred to as an *orthogonal set*. Furthermore, if each wave function in an orthogonal set is also normalized, the set is known as *orthonormal set* (*orthogonal and normalized*).

The probability of finding the particle at the point  $x$  is

$$\psi_n^2 = \frac{2}{l} \sin^2 \left( \frac{n\pi x}{l} \right) \quad (1.4.12)$$

Figure 1.4.2 illustrates the various wave functions, the corresponding energy levels and the probability densities for a few lower quantum numbers  $n$ .

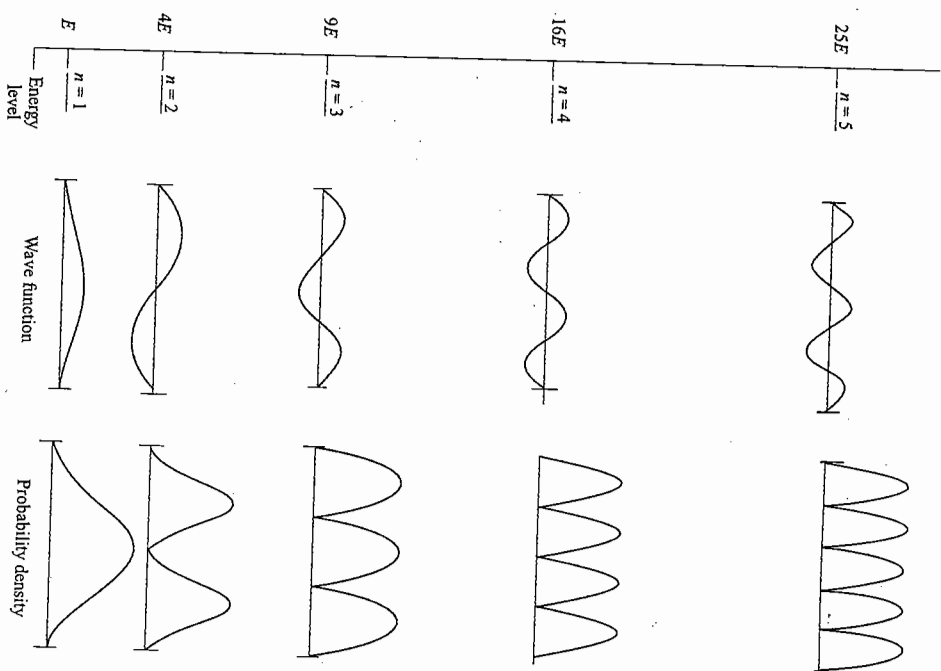


Fig. 1.4.2. The energies, wave functions and probability densities of a particle in a box

### A Few Features of a Particle in a Box

The following features about the wave function and the probability distribution may be pointed out.

- In order that the function  $\psi$  is zero at the walls, the length  $l$  of the box must be an integral multiple of half-wavelengths, i.e.

$$l = n \left( \frac{\lambda}{2} \right) \quad (1.4.13)$$

Equation (1.4.13) can be derived starting from the relation

$$E = n^2 \left( \frac{h^2}{8ml^2} \right), \quad (\text{Eq. 1.4.9})$$

Now  $E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$

Using the de Broglie's relation, we have

$$E = \frac{p^2}{2m} = \frac{(h/\lambda)^2}{2m} = \frac{h^2}{2m\lambda^2} \quad (1.4.14)$$

Equating Eqs (1.4.9) and (1.4.14), we get

$$\frac{h^2}{2m\lambda^2} = \frac{n^2 h^2}{8ml^2}, \quad \text{i.e.} \quad \frac{1}{\lambda^2} = \frac{n^2}{4l^2}$$

or  $l = n \left( \frac{\lambda}{2} \right)$

Thus, the wave functions besides being zero at the walls of the box also have zero values at various points within the box. The number of times the wave function becomes zero, as may be seen from Fig. 1.4.2, is equal to  $(n - 1)$ , where  $n$  is the quantum number. The point at which wave function has a zero value is known as the *node* of the wave function.

- The energy associated with a wave function increases with increase in the number of nodes of the function.
- The symmetry of the wave functions with respect to the centre of the box may be classified into the following two categories:

*Symmetric (or even) function* where  $\psi(x) = \psi(-x)$

*Antisymmetric (or odd) functions* where  $\psi(x) = -\psi(-x)$ .

From Fig. 1.4.2, it may be concluded that the functions  $\psi_1, \psi_3, \psi_5, \dots$  etc., are symmetric functions whereas the functions  $\psi_2, \psi_4, \psi_6, \dots$  are antisymmetric functions with respect to the centre of the box.

- The probability density is not uniform at all positions. This is more pronounced when  $n$  is small. However, the distribution becomes more and more uniform as  $n$  increases and will be completely uniform for very high value of  $n$ . According to classical mechanics, the particle spends, on an average, equal amounts of time at all points and this is achieved only when  $n$  becomes very large. This fact is in agreement with the *correspondence principle*, according to which, the predictions of quantum mechanics for a very large value of  $n$  are identical to those predicted by classical mechanics.

### Free-Electron Model

An important application of particle in a one-dimensional box may be mentioned here. The  $\pi$ -electron in polyene may be identified with the system of particle in a one-dimensional box.<sup>†</sup> The length of the box may be taken as the end-to-end

<sup>†</sup> Although a polyene is not a linear molecule it is assumed, for simplicity, that it is a linear molecule.



distance of the molecule.<sup>†</sup> Thus, knowing  $m_e$  and  $l$ , the electronic energy levels in polyenes can be determined by using Eq. (1.4.9). The  $\pi$ -electrons of polyenes are distributed over these levels following the Pauli exclusion (see Sections 1.12 and 1.14) and aufbau principles. The energy difference between the highest occupied level ( $n$ ) and the lowest unoccupied level ( $n+1$ ) may be identified with the electron transition energy.<sup>‡</sup> The difference between these two levels is

$$\begin{aligned}\Delta E &= E_{n+1} - E_n \\ &= \frac{(n+1)^2 h^2}{8l^2 m} - \frac{n^2 h^2}{8l^2 m} = \frac{h^2}{8l^2 m} \left\{ (n+1)^2 - n^2 \right\} \\ &= (2n+1) \frac{h^2}{8l^2 m} \quad (1.4.15)\end{aligned}$$

For example, in butadiene molecule we will have

$$\begin{aligned}l &= l(\text{single bond-length}) + 2(\text{double bond-length}) + 154 \text{ pm} \\ &= (154 \text{ pm}) + 2(135 \text{ pm}) + 154 \text{ pm} \\ &= 578 \text{ pm} = 5.78 \times 10^{-10} \text{ m}\end{aligned}$$

$$n = \frac{\text{Number of electrons}}{2} = \frac{4}{2} = 2$$

$$\begin{aligned}\text{Hence } \Delta E &= (2 \times 2 + 1) \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8(5.78 \times 10^{-10} \text{ m})^2 (9.11 \times 10^{-31} \text{ kg})} \\ &= 9.02 \times 10^{-19} \text{ J}\end{aligned}$$

$$\begin{aligned}\widetilde{\Delta E} &= \frac{\Delta E}{hc} = \frac{(9.02 \times 10^{-19} \text{ J})}{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})} \\ &= 4.54 \times 10^6 \text{ m}^{-1} = 4.54 \times 10^4 \text{ cm}^{-1}\end{aligned}$$

The corresponding experimental value is  $4.61 \times 10^4 \text{ cm}^{-1}$ .

### Example 1.4.1

Consider a ball of mass 1 g moving with a speed  $1 \text{ cm s}^{-1}$  in a one-dimensional box of edge-length equal to 10 cm. (i) Calculate its kinetic energy and the number  $n$  corresponding to this kinetic energy. (ii) If the ball is to be promoted to the next higher quantum level, then how much of energy is required? From the obtained value, justify that the kinetic energy of a larger mass varies in a continuous manner.

(i) Kinetic energy of the ball is

$$\begin{aligned}E_n &= \frac{1}{2} m v^2 = \left( \frac{1}{2} \right) (10^{-3} \text{ kg}) (10^{-2} \text{ m s}^{-1})^2 \\ &= 0.5 \times 10^{-7} \text{ J}\end{aligned}$$

### Solution

<sup>†</sup> In many cases, the end-to-end distance of the molecule is extended by a half C—C distance on either side of the molecule, i.e. another 154 pm distance is considered.

<sup>‡</sup> See Section 4.1 for the selection rule of particle in a box.

Since  $E_n = n^2 \left\{ \frac{h^2}{8l^2 m} \right\}$ , therefore

$$\begin{aligned}n^2 &= \frac{E_n}{\left( \frac{h^2}{8l^2 m} \right)} = \frac{E_n 8l^2 m}{h^2} = \frac{(0.5 \times 10^{-7} \text{ J})(8 \times 10^{-1} \text{ m})^2 (10^{-3} \text{ kg})}{(6.626 \times 10^{-34} \text{ J s})^2} \\ &= 9.11 \times 10^{54} \\ n &\simeq 3.02 \times 10^{27}\end{aligned}$$

or

(ii) Now  $\Delta E = E_{n+1} - E_n = (2n+1) \left\{ \frac{h^2}{8l^2 m} \right\}$

$$\begin{aligned}&= (2 \times 3.02 \times 10^{27} + 1) \left\{ \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8(10^{-1} \text{ m})^2 (10^{-3} \text{ kg})} \right\} \\ &= 3.32 \times 10^{-35} \text{ J}\end{aligned}$$

It is impossible to observe such a small energy difference and thus  $E$  may be taken to vary in a continuous manner—a characteristic of classical mechanics.

### Example 1.4.2

An electron is confined to a molecule of length of 1 nm (about 5 atoms long). (i) What is its minimum energy? (ii) What is the minimum excitation from this state? (iii) What is the probability of finding it in the region of the molecule lying between  $x = 0$  and  $x = 0.2 \text{ nm}$ ?

(i)  $E_1 = \frac{h^2}{8m_e l^2} = \frac{(6.26 \times 10^{-34} \text{ J s})^2}{8(9.109 \times 10^{-31} \text{ kg})(10^{-9} \text{ m})^2} = 6.025 \times 10^{-20} \text{ J}$

(ii) Now  $E_2 = (4) E_1 = 24.1 \times 10^{-20} \text{ J}$

Hence  $\Delta E = E_2 - E_1 = 4E_1 - E_1 = 3E_1 = 18.075 \times 10^{-20} \text{ J}$

(iii) The probability of finding the electron in the region  $x = 0$  to  $x = 0.2 \text{ nm}$  is

$$\int_{x=0}^{x=0.2 \text{ nm}} \psi_1^2 dx = \frac{2}{l} \int_0^{x=0.2 \text{ nm}} \sin^2(\pi x/l) dx$$

$$= \frac{2}{l} \int_0^{x=0.2 \text{ nm}} \left( \frac{1}{2} \right) [1 - \cos(2\pi x/l)] dx$$

$$= \frac{2}{l} \left[ \frac{x}{2} - \frac{\sin(2\pi x/l)}{2(2\pi/l)} \right]_0^{0.2 \text{ nm}}$$

$$= \frac{2}{(1 \text{ nm})} \left[ \frac{0.2 \text{ nm}}{2} - \frac{(1 \text{ nm})}{4\pi} \sin(0.4\pi) \right]$$

$$= 2 \left\{ 0.1 - \left( \frac{1}{4\pi} \right) (0.9511) \right\} = 2(0.1 - 0.0757) = 0.0486$$

**Problem 1.4.1**

The quantum mechanical operator for the linear momentum in one direction is  $(h/2\pi i)(d/dx)$ . Apply this operator on the eigenfunctions of particle in a one-dimensional box and thus show that these functions are not eigenfunctions of the momentum operator and suggest a possible reason for this.

The expression of eigenfunction for one-dimensional box is given by the expression

$$\psi_n = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right)$$

$$\text{Therefore } \frac{h}{2\pi i} \frac{d}{dx} \psi_n = \frac{h}{2\pi i} \frac{d}{dx} \left( \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \right)$$

$$= \frac{h}{2\pi i} \sqrt{\frac{2}{l}} \frac{n\pi}{l} \cos \frac{n\pi x}{l}$$

$$\text{Since } \frac{h}{2\pi i} \frac{d}{dx} \psi_n \neq (\text{constant}) \psi_n$$

it follows that  $\psi_n$  is not an eigenfunction of the momentum operator.

The particle in the box has only kinetic energy which is related to the momentum  $p$  by  $E = p^2/2m$ . Thus  $p = \pm\sqrt{2mE}$ . Thus for a given value of  $E$ , two directions of the momentum operator are possible and hence it is not uniquely defined.

**Problem 1.4.2**

Evaluate the expectation value of kinetic energy of a particle in a one-dimensional box by making use of Eq. (1.3.13).

The kinetic energy of the particle is given by

$$T = \frac{1}{2} m v^2 = \frac{1}{2} \frac{(mv)^2}{m} = \frac{p^2}{2m}$$

The corresponding quantum mechanical operator is

$$T_{op} = \frac{1}{2m} \left( \frac{h}{2\pi i} \frac{d}{dx} \right)^2 = -\frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2}$$

The wave function for the particle in a one-dimensional box is given by

$$\psi = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right)$$

Since  $\psi$  is normalized function, the expression for the expectation value as given by Eq. (1.3.13) becomes

$$\langle T \rangle = \int_0^l \psi^* (T_{op}) \psi dx$$

Substituting the expression of  $\psi$ , we get

$$\langle T \rangle = \int_0^l \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right) \left( -\frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2} \right) \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right) dx$$

**Problem 1.4.3****Solution**

**Note:**  $T_{op} \psi$  will give  $(\hbar^2/8ml^2) \psi$  indicating that  $\hbar^2/8ml^2$  is an eigenvalue. This is due to the fact that  $\psi$  is an eigenfunction of  $T_{op}$ .

$$\begin{aligned} &= \left(\frac{2}{l}\right) \left(-\frac{h^2}{8\pi^2 m}\right) \int_0^l \sin\left(\frac{n\pi x}{l}\right) \left[\frac{d^2}{dx^2} \sin\left(\frac{n\pi x}{l}\right)\right] dx \\ &= \left(\frac{2}{l}\right) \left(-\frac{h^2}{8\pi^2 m}\right) \left\{ -\left(\frac{n\pi}{l}\right)^2 \int_0^l \sin^2\left(\frac{n\pi x}{l}\right) dx \right\} \\ &= \left(\frac{2}{l}\right) \left(\frac{h^2}{8\pi^2 m}\right) \left(\frac{n\pi}{l}\right)^2 \int_0^l \frac{1}{2} [1 - \cos\left(\frac{2n\pi x}{l}\right)] dx \\ &= \left(\frac{2}{l}\right) \left(\frac{h^2}{8\pi^2 m}\right) \left(\frac{n\pi}{l}\right)^2 \left(\frac{1}{2}\right) l \\ &= \frac{\hbar^2 n^2}{8ml^2} \end{aligned}$$

(a) Apply the variation functions (i)  $x$ , (ii)  $x^2$ , (iii)  $x(l-x)$ , (iv)  $x^2(l-x)^2$  and  $\sin \pi x/l$  to the particle in a box ( $V=0$  for  $0 < x < l$  and  $V=\infty$  elsewhere) and estimate the ground state energy for each. Calculate the per cent error in each case. Given: the correct ground state energy  $= \hbar^2/8ml^2$ . (b) Explain why the functions (i) and (ii) can be used as variation functions for the particle in a box. (c) Explain whether the functions (iii), (iv) and (v) satisfy the variation principle or not.

(a) The ground state energy can be computed from the relation

$$\langle E \rangle = \frac{\langle \psi | H_{op} | \psi \rangle}{\langle \psi | \psi \rangle}$$

where  $H_{op}$  the Hamiltonian operator, is given by the relation

$$H_{op} = -\frac{\hbar^2}{8\pi^2 m} \frac{d^2}{dx^2}$$

Thus, we have

$$(i) \quad \langle E \rangle = \frac{\left\langle x \left| -\frac{\hbar^2}{8\pi^2 m} \frac{d^2}{dx^2} \right| x \right\rangle}{\langle x | x \rangle} = 0$$

$$\text{Per cent error} = \frac{0 - (\hbar^2/8ml^2)}{(\hbar^2/8ml^2)} \times 100 = -100$$

$$(ii) \quad \langle E \rangle = \frac{\left\langle x^2 \left| -\frac{\hbar^2}{8\pi^2 m} \frac{d^2}{dx^2} \right| x^2 \right\rangle}{\langle x^2 | x^2 \rangle} = -\frac{\hbar^2}{8\pi^2 m} \left[ \frac{\int_0^l x^2 dx}{\int_0^l x^4 dx} \right]$$

$$= -\frac{\hbar^2}{8\pi^2 m} (2) \left[ \frac{l^3/3}{l^5/5} \right] = -\frac{\hbar^2}{8\pi^2 m} \left[ \frac{10}{3\pi^2} \right]$$

$$\text{Per cent error} = \frac{(h^2/8ml^2)(-10/3\pi^2) - (h^2/8ml^2)}{(h^2/8ml^2)} \times 100$$

$$= \frac{-(10/3\pi^2) - 1}{1} \times 100 = -133.75$$

$$\langle x(l-x) \rangle = \frac{\int_0^l \frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2} x(l-x) dx}{\int_0^l x(l-x) |x(l-x)| dx}$$

$$= \frac{h^2}{8\pi^2 m} (2) \left[ \frac{\int_0^l x(l-x) dx}{\int_0^l x^2(l-x)^2 dx} \right] = \frac{h^2}{8\pi^2 m} (2) \left[ \frac{(l^3/2) - (l^3/3)}{(l^5/3) + (l^5/5) - (l^5/2)} \right]$$

$$= \frac{h^2}{8ml^2} \left( \frac{10}{\pi^2} \right)$$

$$\text{Per cent error} = \frac{(h^2/8ml^2)(10/\pi^2) - (h^2/8ml^2)}{(h^2/8ml^2)} \times 100 = +1.24$$

$$\langle x^2(l-x)^2 \rangle = \frac{\int_0^l \frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2} x^2(l-x)^2 dx}{\int_0^l x^2(l-x)^2 |x^2(l-x)^2| dx}$$

$$= \left( -\frac{h^2}{8\pi^2 m} \right) \left[ \frac{\int_0^l x^2(l-x)^2(2l^2 + 12x^2 - 12lx) dx}{\int_0^l x^4(l-x)^4 dx} \right]$$

$$= \left( -\frac{h^2}{8\pi^2 m} \right) \left[ \frac{-2l^7/105}{l^9/630} \right] = \left( \frac{h^2}{8ml^2} \right) \left( \frac{12}{\pi^2} \right)$$

$$\text{Per cent error} = \frac{(h^2/8ml^2)(12/\pi^2) - (h^2/8ml^2)}{(h^2/8ml^2)} \times 100 = +21.49$$

$$\langle \sin(\pi x/l) \rangle = \frac{\int_0^l \frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2} \sin(\pi x/l) dx}{\int_0^l \sin(\pi x/l) |\sin(\pi x/l)| dx} = \left( -\frac{h^2}{8\pi^2 m} \right) \left( -\frac{\pi^2}{l^2} \right)$$

$$= \frac{h^2}{8ml^2}$$

$$\text{Per cent error} = 0$$

#### Problem 1.4.4

#### Solution

Evaluate the expectation values of  $x$ ,  $x^2$ ,  $p$  and  $p^2$  for a particle in a one-dimensional box of length  $l$  and show that the product of root mean square uncertainties in  $p$  and  $x$  is greater than  $h/4\pi$ .

For a particle in a one-dimensional box, we have

$$\psi_n = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right)$$

Since  $\psi_n$  is the normalized wave function, we will have

$$\begin{aligned} \langle x \rangle &= \int_0^l \psi |x| \psi dx \\ &= \frac{2}{l} \int_0^l x \sin^2\left(\frac{n\pi}{l} x\right) dx = \frac{2}{l} \int_0^l x \left[ \frac{1 - \cos\left(\frac{2n\pi}{l} x\right)}{2} \right] dx \\ &= \left(\frac{2}{l}\right) \left(\frac{l^2}{4}\right) = \frac{l}{2} \end{aligned}$$

$$\langle x^2 \rangle = \frac{2}{l} \int_0^l x^2 \sin^2\left(\frac{n\pi}{l} x\right) dx$$

$$= \frac{2}{l} \int_0^l x^2 \left[ \frac{1 - \cos\left(\frac{2n\pi}{l} x\right)}{2} \right] dx = \frac{1}{l} \left[ \frac{l^3}{3} - \frac{l^3}{2n^2\pi^2} \right]$$

$$\langle p \rangle = \int_0^l \psi \left| \frac{h}{2\pi i} \frac{d}{dx} \right| \psi dx$$

$$= \frac{h}{2\pi i} \int_0^l \left( \frac{2}{l} \right) \sin\left(\frac{n\pi x}{l}\right) \left| \frac{d}{dx} \right| \sin\left(\frac{n\pi x}{l}\right) dx$$

(b) The functions  $x$  and  $x^2$  cannot be used as the variation functions since they do not satisfy the boundary conditions of  $\psi = 0$  at  $x = 0$  and  $x = l$ .

(c) The variational theorem may be stated as follows.

If a well-behaved approximate wave function is employed in evaluating the expectation value of a system then the value so obtained will always be algebraically equal to or greater than the true energy of the system.

Since the functions (i) and (ii) are not well-behaved functions (explained in part b), the expectation values obtained by these functions are lower than the correct value. Functions (iii), (iv) and (v) are well-behaved functions, the expectation values obtained by these functions come out to be larger than (for functions iii and iv) and equal to (for function v) the correct value. Hence, the variation theorem is satisfied by these functions.

$$= \frac{h}{2\pi i} \left( \frac{\pi}{l} \right) \int_0^l \left( \frac{2}{l} \right) \sin \left( \frac{\pi x}{l} \right) \cos \left( \frac{\pi x}{l} \right) dx$$

$$= 0$$

$$\langle p^2 \rangle = \int_0^l \left\{ \psi \left[ \left( \frac{h}{2\pi i} \frac{d}{dx} \right)^2 \right] \psi \right\} dx$$

$$= \left( -\frac{h^2}{4\pi^2} \right) \int_0^l \left\{ \left( \frac{2}{l} \right) \sin \left( \frac{\pi x}{l} \right) \frac{d^2}{dx^2} \sin \left( \frac{\pi x}{l} \right) \right\} dx$$

$$= \left( \frac{h^2}{4\pi^2} \right) \left( \frac{\pi}{l} \right)^2 \int_0^l \left( \frac{2}{l} \right) \sin^2 \left( \frac{\pi x}{l} \right) dx$$

$$= \left( \frac{h^2}{4\pi^2} \right) \left( \frac{\pi}{l} \right)^2 (1) = \frac{n^2 h^2}{4l^2} = 2mE$$

$$\text{Now } \langle \Delta p \rangle^2 = \langle p^2 \rangle - \langle p \rangle^2 = \langle p^2 \rangle = \frac{n^2 h^2}{4l^2}$$

$$\langle \Delta x \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2 = \left( \frac{l^2}{3} - \frac{l^2}{2\pi^2} \right) - \left( \frac{l}{2} \right)^2 = \left( \frac{l^2}{12} - \frac{l^2}{2\pi^2} \right)$$

$$\begin{aligned} \langle \Delta p \rangle^2 \langle \Delta x \rangle^2 &= \left( \frac{n^2 h^2}{4l^2} \right) \left( \frac{l^2}{12} - \frac{l^2}{2\pi^2} \right) = \left( \frac{n^2 h^2}{4} \right) \left( \frac{1}{12} - \frac{1}{2\pi^2} \right) \\ &= \left( \frac{h^2}{16\pi^2} \right) \left( \frac{\pi^2}{3} - 2 \right) \end{aligned}$$

$$\text{Hence } \Delta p \Delta x = \frac{h}{4\pi} \sqrt{\frac{\pi^2}{3} - 2} > \frac{h}{4\pi}; \text{ since } \pi^2/3 \text{ is always greater than } 2.$$

**Problem 1.4.5**

$$\delta E \Delta t \geq \frac{h}{4\pi}$$

Making use of the expression  $\Delta p \Delta x \geq h/4\pi$ , show that for a free particle where  $\delta E$  and  $\Delta t$  are the minimum uncertainties in energy and duration of measurement of velocity, respectively.

For a free particle, the energy expression is

$$E = \frac{1}{2} m v^2 = \frac{p^2}{2m}$$

The uncertainty in energy will be given by

$$\delta E = \frac{p}{m} \delta p$$

where  $\delta p$  is the uncertainty in  $p$ . Now  $p/m$ , which is velocity, may be measured by determining the distance  $\Delta x$  traversed in time  $\Delta t$ , such that

$$\frac{p}{m} = \frac{\Delta x}{\Delta t}$$

If  $\Delta x$  is the maximum uncertainty in position of the particle during the measurement of  $p$ , then the minimum uncertainty in the value of  $p$  will be

$$\delta p \geq \left( \frac{h}{4\pi} \right) \frac{1}{\Delta x}$$

$$\begin{aligned} \text{Hence } \delta E &= \frac{p}{m} \delta p = \frac{\Delta x}{\Delta t} \delta p \geq \left( \frac{h}{4\pi} \right) \frac{1}{\Delta t} \\ \text{or } \delta E \Delta t &\geq \frac{h}{4\pi} \end{aligned}$$

**Problem 1.4.6**

A particle of mass  $m$  is confined to a one-dimensional box with the origin at the centre of the box. The box extends from  $-l/2$  to  $+l/2$ . The potential energy is

$$V(x) = \begin{cases} 0, & -l/2 < x < l/2 \\ \infty, & |x| \geq l/2 \end{cases}$$

(a) Write the Schrödinger equation for the system showing separate equations for the inside and the outside of the box.

(b) Assume a solution (inside the box) of the form

$$\psi(x) = A \sin(\alpha x) + B \cos(\alpha x)$$

find out its correct form by making use of boundary conditions.

(c) Derive the energy expression of the particle.

(a) The Schrödinger equations are

(i) Inside the box

$$-\frac{h^2}{8\pi^2 m} \frac{d^2 \psi}{dx^2} = E \psi$$

(ii) Outside the box

$$-\frac{h^2}{8\pi^2 m} \frac{d^2 \psi}{dx^2} + \infty \psi = E \psi$$

(b) Substituting the boundary conditions

$$\psi(+l/2) = 0 \text{ and } \psi(-l/2) = 0$$

in the expression

$$\psi(x) = A \sin(\alpha x) + B \cos(\alpha x)$$

we get

$$A \sin(\alpha l/2) + B \cos(\alpha l/2) = 0$$

$$\text{and } -A \sin(\alpha l/2) + B \cos(\alpha l/2) = 0$$

On adding and subtracting the above two equations, we get

$$A \sin(\alpha l/2) = 0$$

$$B \cos(\alpha l/2) = 0$$

For Eq. (3), we must have either  $A = 0$  or  $\alpha l/2 = n'\pi$  with  $n' = 1, 2, 3, \dots$ , and for Eq. (4), we must have either  $B = 0$  or  $\alpha l/2 = n''\pi$  with  $n'' = 1/2, 3/2, 5/2, \dots$ .

For  $A = 0$ , the wave function will be given by

$$\psi = B \cos(\alpha x) \quad (5)$$

where  $\alpha = 2n''\pi/l = n\pi/l$  with  $n = 1, 3, 5, \dots$  (odd number only).

For  $B = 0$ , the wave function will be given by

$$\psi = A \sin(\alpha x) \quad (6)$$

where  $\alpha = 2n'\pi/l = n\pi/l$  with  $n = 2, 4, 6, \dots$  (even number only). Equations (5) and (6) may be combined to give

$$\begin{aligned} \psi &= A \sin\left(\frac{n\pi}{l}x\right); & n \text{ even} \\ &= B \cos\left(\frac{n\pi}{l}x\right); & n \text{ odd} \end{aligned}$$

(c) On substituting either Eq. (5) or Eq. (6) in Eq. (1), and carrying out the desired differentiation, we get

$$E = \frac{\hbar^2 n^2}{8ml^2}; \quad n = 1, 2, 3, \dots$$

[Note: Experimentally observable properties do not depend on the choice of the place of origin, i.e. whether it is located at the wall or in between the one-dimensional box. This is to be expected since the particle knows only the length of box where it has to move.]

Alternatively, we may solve the Schrödinger equation after carrying out the following transformation.

Let  $X = x + l/2$  such that  $X = 0$  at  $x = -l/2$  and  $X = l$  at  $x = l/2$ .

Since  $\frac{d}{dx} = \left(\frac{dX}{dx}\right)\left(\frac{d}{dX}\right) = \frac{d}{dX}$ , the Schrödinger equation becomes

$$-\frac{\hbar^2}{8\pi^2m} \frac{d^2\psi}{dX^2} = E\psi$$

The solutions of the equation is given by

$$\psi = A \sin(\alpha X) + B \cos(\alpha X)$$

Making use of boundary conditions ( $\psi = 0$  at  $X = 0$  and  $X = l$ ), this reduces to

$$\psi = A \sin\left(\frac{n\pi}{l}X\right); \quad n = 1, 2, 3, \dots$$

$$\text{i.e.} \quad \psi = A \sin\left\{\frac{n\pi}{l}(x + l/2)\right\}; \quad n = 1, 2, 3, \dots$$

### THREE-DIMENSIONAL BOX

For a particle in a three-dimensional box, the form of Schrödinger equation is

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi + \frac{8\pi^2m}{h^2}E\psi = 0 \quad (1.4.16)$$

where the function  $\psi$  will depend on the three independent variables  $x, y$  and  $z$ . If an operator contains different terms each depending upon independent coordinate, then the wave function can be written as the product of different wave functions each involving individual independent coordinate. Guided by this, we write the function as a product of three wave functions each involving only one independent variable of  $x, y$  and  $z$ , respectively. Thus, we have

$$\psi(x, y, z) = X(x)Y(y)Z(z) \quad (1.4.17)$$

where  $X(x)$ ,  $Y(y)$  and  $Z(z)$  are three functions.

Substituting Eq. (1.4.17) in Eq. (1.4.16), we get

$$\nabla^2(XYZ) + \frac{8\pi^2m}{h^2}EXYZ = 0$$

$$\text{or} \quad \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)(XYZ) + \frac{8\pi^2m}{h^2}E(XYZ) = 0$$

$$\text{or} \quad YZ\left(\frac{d^2}{dx^2}X\right) + XZ\left(\frac{d^2}{dy^2}Y\right) + XY\left(\frac{d^2}{dz^2}Z\right) + \frac{8\pi^2m}{h^2}EXYZ = 0 \quad (1.4.18)$$

Dividing by  $XYZ$ , we have

$$\frac{1}{X}\left(\frac{d^2}{dx^2}X\right) + \frac{1}{Y}\left(\frac{d^2}{dy^2}Y\right) + \frac{1}{Z}\left(\frac{d^2}{dz^2}Z\right) = -\frac{8\pi^2m}{h^2}E = -\alpha^2 \quad (1.4.19)$$

The term  $\alpha^2$  in the above equation is a constant quantity. Hence, the sum of the three terms on the left side of Eq. (1.4.19) must also be a constant quantity. If we change the value of  $x$  (or  $y$  or  $z$ ) keeping the other two variables constants, even then the above constancy has to be satisfied. This is possible only when each term is independent of the other terms and each is equal to a constant quantity so that the sum of three constants is equal to  $\alpha^2$ . Thus, we write

$$\frac{1}{X}\frac{d^2}{dx^2}X = -\alpha_x^2 \quad (1.4.20)$$

$$\frac{1}{Y}\frac{d^2}{dy^2}Y = -\alpha_y^2 \quad (1.4.21)$$

$$\frac{1}{Z}\frac{d^2}{dz^2}Z = -\alpha_z^2 \quad (1.4.22)$$

$$\text{where} \quad \alpha_x^2 = \frac{8\pi^2m}{h^2}E_x \quad (1.4.23)$$

$$\alpha_y^2 = \frac{8\pi^2 m}{h^2} E_y \quad (1.4.24)$$

$$\alpha_z^2 = \frac{8\pi^2 m}{h^2} E_z \quad (1.4.25)$$

with  $\alpha^2 = \alpha_x^2 + \alpha_y^2 + \alpha_z^2$  (1.4.26)

and  $E = E_x + E_y + E_z$  (1.4.27)

Now, we have three separate equations to be solved, each of them has a form of one-dimensional box. Thus, the normalized wave function of a three-dimensional box is

$$\begin{aligned} \psi = XYZ &= \left( \sqrt{\frac{2}{l_x}} \sin \frac{n_x \pi}{l_x} x \right) \left( \sqrt{\frac{2}{l_y}} \sin \frac{n_y \pi}{l_y} y \right) \left( \sqrt{\frac{2}{l_z}} \sin \frac{n_z \pi}{l_z} z \right) \\ &= \sqrt{\frac{8}{l_x l_y l_z}} \sin \left( \frac{n_x \pi}{l_x} x \right) \sin \left( \frac{n_y \pi}{l_y} y \right) \sin \left( \frac{n_z \pi}{l_z} z \right) \end{aligned} \quad (1.4.28)$$

The constants  $\alpha_x$ ,  $\alpha_y$  and  $\alpha_z$  will be given by

$$\alpha_x = \frac{n_x \pi}{l_x}, \quad \alpha_y = \frac{n_y \pi}{l_y} \quad \text{and} \quad \alpha_z = \frac{n_z \pi}{l_z} \quad (1.4.29)$$

and thus the total energy is

$$E = E_x + E_y + E_z = \frac{h^2}{8m} \left( \frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) \quad (1.4.30)$$

There are three quantum numbers, one each for every degree of freedom.

### Example 1.4.3

The ground state translational energy of a particle in a one-dimensional box of 300 pm length is about 4 eV. Suppose that the same particle is moving in a three-dimensional cubic box of 100 pm on the side. Estimate the ground-state energy of the particle in the three-dimensional box.

The ground-state energy in one-dimensional box is

$$E_1 = \frac{(1)^2 h^2}{8ml^2}$$

Now  $l = 300$  pm. Therefore

$$E_1 = \frac{h^2}{8m(300 \text{ pm})^2} = 4 \text{ eV}$$

Hence  $\frac{h^2}{8m} = (4 \text{ eV}) (300 \text{ pm})^2$

The energy expression in a three-dimensional box is

$$E'_1 = \frac{h^2}{8m} \left( \frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right)$$

For the ground state of particle in a three-dimensional box,

$$n_x = n_y = n_z = 1$$

and it is given that

$$l_x = l_y = l_z = 100 \text{ pm}$$

$$\begin{aligned} \text{Thus } E'_1 &= \frac{h^2}{8ml^2} (3) = \frac{h^2}{8m} \cdot \frac{3}{(100 \text{ pm})^2} = \{(4 \text{ eV}) (300 \text{ pm})^2\} \left\{ \frac{3}{(100 \text{ pm})^2} \right\} \\ &= 4 \times 9 \times 3 \text{ eV} = 108 \text{ eV} \end{aligned}$$

An electron confined to a one-dimensional box of length 0.14 nm has a ground-state energy corresponding to the radiation of wavelength about 70 nm. Benzene, as a rough approximation, may be considered to be a two-dimensional box that encompasses the regular hexagonal shape. The C—C bond length in benzene is 0.14 nm, so that side of the box would be about 0.28 nm. Estimate wavelength for transition from ground state to first excited state of benzene, assuming that it is  $\pi$ -bonding electrons that are involved. For the one-dimensional box,

$$E = \frac{h^2}{8ml^2} n^2$$

Thus, the ground state energy  $E_1$  in a one-dimensional box of length 0.14 nm is

$$E_1 = \frac{h^2}{8m(0.14 \text{ nm})^2}$$

For the two-dimensional square box,

$$E_2 = \frac{h^2}{8ml^2} (n_1^2 + n_2^2)$$

Now since  $l = 0.28$  nm, we have

$$E_2 = \frac{h^2}{8m(2 \times 0.14 \text{ nm})^2} (n_1^2 + n_2^2) = \frac{E_1}{4} (n_1^2 + n_2^2)$$

The various energy levels are as follows.

$n_1$	$n_2$	$E_2$
1	1	$E_1/2$
2	1	$(5/4) E_1$
1	2	$(5/4) E_1$
2	2	$2 E_1$

degenerate

The first three energy levels will be doubly occupied in the ground state and hence the first excited state is obtained when the electron is promoted from  $n_1 = 1$ ,  $n_2 = 2$  state to  $n_1 = 2$ ,  $n_2 = 2$  state. Thus

$$\Delta E = 2E_1 - \frac{5}{4}E_1 = \frac{3}{4}E_1$$

Since the wavelength is inversely proportional to energy, the corresponding wavelength would be  $(4/3)\lambda$ , i.e.

$$\frac{4}{3} \times 70 \text{ nm} = 93 \text{ nm}$$

### Example 1.4.5

A cubic box of edge-length 1.2 nm contains 10 electrons. Applying the simple particle-in-a-box theory, calculate the value of  $\Delta E$  for the first excited state of this system.

The energy expression is given as

$$\begin{aligned} E &= \frac{h^2}{8ml^2} (n_1^2 + n_2^2 + n_3^2) \\ &= \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8(9.11 \times 10^{-31} \text{ kg})(1.2 \times 10^{-9} \text{ m})^2} (n_1^2 + n_2^2 + n_3^2) \\ &= (4.1834 \times 10^{-20} \text{ J}) (n_1^2 + n_2^2 + n_3^2) \end{aligned}$$

A few energy levels are shown in the following.

Quantum numbers			$E/J$	Distribution of 10 electrons in the energy levels	
$n_1$	$n_2$	$n_3$			
1	1	1	$(4.1834 \times 10^{-20})$ (3)	$\uparrow\downarrow$	
1	1	2	$(4.1834 \times 10^{-20})$ (6)	$\uparrow\downarrow$	$\uparrow\downarrow$
1	2	1		$\uparrow\downarrow$	$\uparrow\downarrow$
2	1	1		$\uparrow\downarrow$	$\uparrow\downarrow$
1	2	2	$(4.1834 \times 10^{-20})$ (9)	$\uparrow$	$\uparrow$
2	1	2		$\uparrow$	$\uparrow$
2	2	1		$\uparrow$	$\uparrow$
3	1	1	$(4.1834 \times 10^{-20})$ (11)		

The ten electrons can be distributed over the energy levels following the aufbau principle, Pauli exclusion principle, and Hund's rule. The first excited state is obtained when the electron is promoted from the triply degenerate level of energy  $9(4.1834 \times 10^{-20} \text{ J})$  to the level of energy  $11(4.1834 \times 10^{-20} \text{ J})$ . Hence

$$\Delta E = 2(4.1834 \times 10^{-20} \text{ J}) = 8.366 \times 10^{-20} \text{ J}$$

Determine the energy required for a transition from the  $n_x = n_y = n_z = 1$  to  $n_x = n_y = 1$ ,  $n_z = 2$  state for (a) an argon atom (molar mass =  $39.95 \text{ g mol}^{-1}$ ) in a cubic container with a 1.0 cm side, (b) an electron ( $m_e = 9.11 \times 10^{-28} \text{ g}$ ) in a cubic hole of a crystal with  $10^{-8} \text{ cm}$  edge-length.

(a) The mass of one argon atom is

$$m = \frac{(39.95 \times 10^{-3} \text{ kg mol}^{-1})}{(6.023 \times 10^{23} \text{ mol}^{-1})} = 6.633 \times 10^{-26} \text{ kg}$$

$$\begin{aligned} \text{Now } E_{1,1,1} &= \frac{h^2}{8ml^2} (n_x^2 + n_y^2 + n_z^2) = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8(6.633 \times 10^{-26} \text{ kg})(10^{-2} \text{ m})^2} (1^2 + 1^2 + 1^2) \\ &= (8.274 \times 10^{-39} \text{ J}) \quad (3) \\ &= 2.482 \times 10^{-38} \text{ J} \end{aligned}$$

$$\begin{aligned} E_{1,1,2} &= (8.274 \times 10^{-39} \text{ J}) (1^2 + 1^2 + 2^2) = (8.274 \times 10^{-39} \text{ J}) \quad (6) \\ &= 4.964 \times 10^{-38} \text{ J} \end{aligned}$$

$$\begin{aligned} \text{Hence } \Delta E &= E_{1,1,2} - E_{1,1,1} = (4.964 \times 10^{-38} \text{ J} - 2.482 \times 10^{-38} \text{ J}) \\ &= 2.482 \times 10^{-38} \text{ J} \end{aligned}$$

(b) In this case, we have

$$\begin{aligned} E_{1,1,1} &= \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8(9.11 \times 10^{-31} \text{ kg})(10^{-10} \text{ m})^2} \times 3 = (6.024 \times 10^{-18} \text{ J}) \quad (3) \\ &= 1.8072 \times 10^{-17} \text{ J} \end{aligned}$$

$$\text{and } E_{1,1,2} = (6.024 \times 10^{-18} \text{ J}) \quad (6) = 3.6144 \times 10^{-17} \text{ J}$$

$$\begin{aligned} \text{Thus } \Delta E &= (3.6144 \times 10^{-17} \text{ J} - 1.8072 \times 10^{-17} \text{ J}) \\ &= 1.8072 \times 10^{-17} \text{ J} \end{aligned}$$

The average kinetic energy of a gas molecule is  $(3/2)kT$ , where  $k$  is the Boltzmann constant. What will have to be the average value of  $(n_x^2 + n_y^2 + n_z^2)$  in order that atom of He may possess a temperature of 300 K when confined in a cubical box 10 nm on edge?

The energy expression of a three-dimensional box is

$$E = \frac{h^2}{8ml^2} (n_x^2 + n_y^2 + n_z^2)$$

Since  $l = 10 \text{ nm}$ , we have for He atom

$$\begin{aligned} E &= \frac{(6.626 \times 10^{-34} \text{ J s})^2}{(8) \{0.004 \text{ kg} / (6.023 \times 10^{23})\} (10^{-8} \text{ m})^2} (n_x^2 + n_y^2 + n_z^2) \\ &= (8.263 \times 10^{-26} \text{ J}) (n_x^2 + n_y^2 + n_z^2) \end{aligned}$$

Now, the average kinetic energy at 300 K is

$$\bar{E} = \frac{3}{2} kT = \frac{3}{2} \left( \frac{R}{N_A} \right) T = \frac{3}{2} \left( \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}} \right) (300 \text{ K})$$

$$= 6.2117 \times 10^{-21} \text{ J}$$

Equating the above energy with  $E$ , we get

$$(8.263 \times 10^{-26} \text{ J}) (n_x^2 + n_y^2 + n_z^2) = 6.2117 \times 10^{-21} \text{ J}$$

$$n_x^2 + n_y^2 + n_z^2 = \frac{6.2117 \times 10^{-21} \text{ J}}{8.263 \times 10^{-26} \text{ J}} = 75.175$$

## 1.5 QUANTIZATION OF VIBRATIONAL ENERGY

### Harmonic Oscillator

For the sake of simplicity, we treat here only the simple harmonic motion of a single particle which oscillates to and fro about its equilibrium position. In harmonic motion, the restoring force  $F$  acting on the particle is proportional to the displacement  $x$  from the equilibrium position (Fig. 1.5.1).

Thus  $F \propto x$

$$\text{or } F = -k_f x \quad (1.5.1)$$

where  $k_f$  is a constant, called the force constant, and is a measure of the stiffness of the spring. A strong inflexible spring will have a larger value of  $k_f$  and a weaker spring will have a lesser value of  $k_f$ . The negative sign in Eq. (1.5.1) indicates that the restoring force always acts in the opposite direction of the displacement.

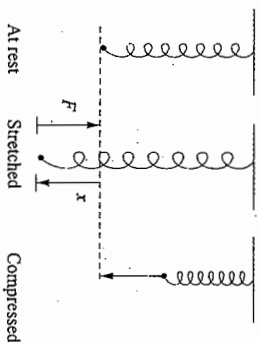


Fig. 1.5.1 Classical treatment of harmonic motion

### Classical Treatment

In classical mechanics, the above vibrational motion can be described in terms of Newton's second law of motion, according to which, we have

$$F = ma = m \frac{d^2x}{dt^2} \quad (1.5.2)$$

Equating Eqs (1.5.1) and (1.5.2), we get

$$m \frac{d^2x}{dt^2} = -k_f x \quad (1.5.3)$$

### Classical Frequency of Oscillation

The solution of Eq. (1.5.3) has a form

$$x = A \sin (2\pi\nu_0 t) \quad (1.5.4a)$$

$$\text{or } x = A \cos (2\pi\nu_0 t) \quad (1.5.4b)$$

where  $A$  is the maximum displacement of the vibration and  $\nu_0$  is the frequency of vibration.

The value of  $\nu_0$  depends on the mass of the particle and the force constant of the spring. The relation connecting these can be derived as follows.

Evaluating the second differential of Eq. (1.5.4a) and substituting in Eq. (1.5.3), we get

$$m[-A(2\pi\nu_0)^2 \sin (2\pi\nu_0 t)] = -k_f A \sin (2\pi\nu_0 t)$$

$$\text{or } m(2\pi\nu_0)^2 = k_f$$

$$\text{or } \nu_0 = \frac{1}{2\pi} \sqrt{\frac{k_f}{m}} \quad (1.5.5)$$

The potential energy of the particle at any instant can be evaluated from the expression

$$F = -dV/dx, \text{ i.e. } dV = -F dx$$

Substituting  $F$  from Eq. (1.5.1), we have

$$dV = k_f x dx$$

which on integrating gives

$$\int_0^x dV = k_f \int_0^x x dx$$

$$(1.5.6)$$

$$\text{i.e. } V = k_f \frac{x^2}{2}$$

The variation in potential energy with the displacement  $x$  is shown in Fig. 1.5.2.

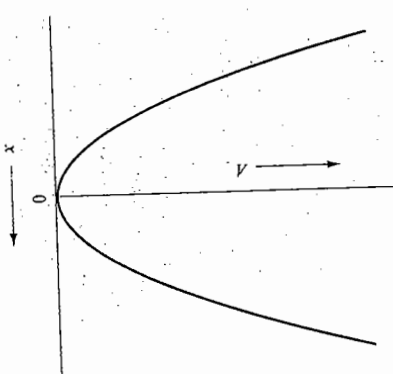


Fig. 1.5.2 The parabolic potential energy for the harmonic oscillator



### Total Energy of the Oscillator

The momentum of the particle at any instant is

$$p = mv = m \frac{dx}{dt} = mA(2\pi\nu_0) \cos(2\pi\nu_0 t) \quad (1.5.7)$$

The total energy of the particle at any instant is

$$\begin{aligned} E &= T + V \\ &= \frac{1}{2} mv^2 + V = \frac{p^2}{2m} + \frac{k_f x^2}{2} \\ &= \frac{\{mA(2\pi\nu_0) \cos(2\pi\nu_0 t)\}^2}{2m} + \frac{k_f}{2} \{A \sin(2\pi\nu_0 t)\}^2 \\ &= \frac{m^2 A^2 (k_f/m) \cos^2(2\pi\nu_0 t)}{2m} + \frac{k_f}{2} A^2 \sin^2(2\pi\nu_0 t) \\ &= \frac{1}{2} k_f A^2 \cos^2(2\pi\nu_0 t) + \frac{1}{2} k_f A^2 \sin^2(2\pi\nu_0 t) \end{aligned}$$

$$\text{or } E = \frac{1}{2} k_f A^2 \quad (1.5.8)$$

The particle executing simple harmonic motion will have the following characteristics.

- The frequency of oscillation is a characteristic of the system which depends only on  $k_f$  and  $m$ , and not on the amplitude of vibration (Eq. 1.5.5). Thus, whatever may be the amplitude the particle will oscillate with the same frequency.
- The potential energy of the particle, besides depending on  $k_f$ , depends on the square of the displacement (Eq. 1.5.6). Thus, the variation of potential energy with displacement  $x$  is of parabolic in nature (Fig. 1.5.2).
- The total energy of the particle, besides depending upon  $k_f$ , depends on the square of the amplitude of the vibration (Eq. 1.5.8). Since the oscillating particle can possess any amplitude, it is obvious that the total energy of the particle will vary in a continuous manner.
- Classically speaking, the time spent at any position during vibration will depend on the velocity of the particle at that instant; larger the velocity, lesser the time spent and vice versa. Since, the total energy of an oscillator depends only on the amplitude of the vibration (Eq. 1.5.8), it is obvious that the sum of kinetic and potential energies remains the same at any instant of vibration. The potential energy increases as the displacement  $x$  is increased (Eq. 1.5.6) and it attains a maximum value equal to the total energy at the two extremes of the vibration. Consequently, the kinetic energy of the particle decreases as the displacement  $x$  is increased and it has a zero value at the two extremes of the vibration. At equilibrium position ( $x = 0$ ), the potential energy is zero and the particle carries only kinetic energy equal to the total energy. Thus, we have

### Quantum Mechanical Treatment

At  $x = 0$ ; kinetic energy is maximum or velocity of the oscillator is maximum. At  $x = A$ ; kinetic energy is zero or velocity of the oscillator is zero.

Since the velocity of the oscillator at  $x = 0$  is maximum and is zero at the extremes of vibration, it is expected that the particle will spend maximum time at the extremes and the minimum at the equilibrium position during the course of its vibration.

The Schrödinger equation of the particle executing simple harmonic motion is given by

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} \left( E - \frac{1}{2} k_f x^2 \right) \psi = 0 \quad (1.5.9)$$

The solution of this equation by the power series method and the factorization method is described in Annexure II at the end of the chapter. The final results are as follows.

1. The energy of an oscillator is quantized and is given by the expression

$$E_v = \left( v + \frac{1}{2} \right) h\nu_0 = \left( v + \frac{1}{2} \right) \frac{h}{2\pi} \sqrt{\frac{k_f}{m}} \quad (1.5.10)$$

where  $\nu_0$  is the classical frequency of the oscillator and  $v$  is the vibrational quantum number which can have only integral values including zero, i.e.  $v = 0, 1, 2, 3, \dots$

2. The acceptable normalized wave functions of Eq. (1.5.9) are given by the expression

$$\psi_v = \left( \frac{\sqrt{\alpha}}{2^v v! \sqrt{\pi}} \right)^{1/2} H_v \exp \left( -\frac{1}{2} \alpha y^2 \right) \quad (1.5.11)$$

where  $y = \sqrt{\alpha}x$ . The symbol  $\alpha$  in this expression is given by

$$\alpha = \frac{m\omega}{h/2\pi} \quad \text{where } \omega = \sqrt{k_f/m} \quad (1.5.12)$$

$H_v$  in Eq. (1.5.11) represents the Hermite polynomials. The first few Hermite polynomials are listed in Table 1.5.1.

**Table 1.5.1 The First Few Hermite Polynomials**

$H_0 = 1$	$H_4 = 16y^4 - 48y^2 + 12$
$H_1 = 2y$	$H_5 = 32y^5 - 160y^3 + 120y$
$H_2 = 4y^2 - 2$	$H_6 = 64y^6 - 480y^4 + 720y^2 - 120$
$H_3 = 8y^3 - 12y$	

\*For a diatomic molecule, the mass  $m$  is replaced by reduced mass  $\mu [= m_1 m_2 / (m_1 + m_2)]$ .

### Depiction of Energies, Wave Functions and Probability Densities

Figure 1.5.3 depicts the first few wave functions, the corresponding energies and the probability densities of a harmonic oscillator.

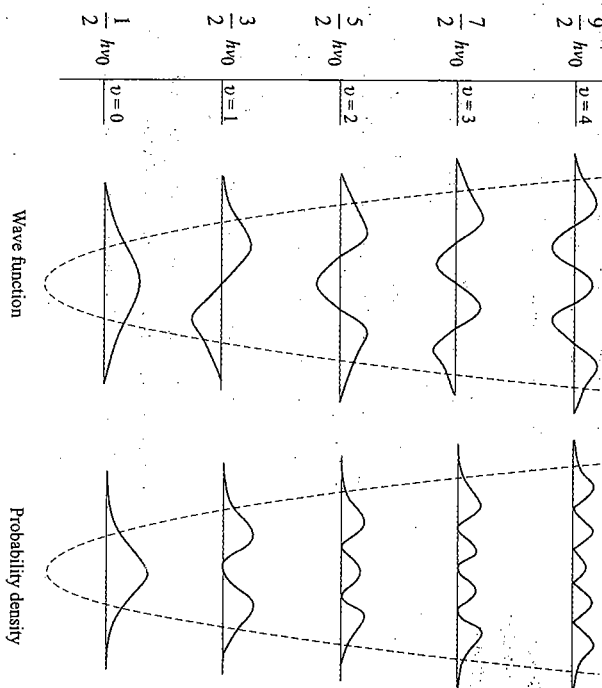


Fig. 1.5.3 The energies, wave functions and probability densities of a harmonic oscillator

### Quantum Characteristics of a Harmonic Oscillator

A few important features shown in Fig. 1.5.3 may be highlighted here.

- The vibrational energies are quantized, and the separation between the successive energy levels is the same for all values of  $v$ , i.e.

$$\Delta E = E_{v+1} - E_v = h\nu$$

- The particle is associated with the zero point energy of  $(1/2)h\nu$  (energy in the lowest vibrational level,  $v = 0$ ). This implies that the particle can never be standstill. This is contrary to the classical picture where the particle has zero potential energy at its equilibrium position, i.e. at  $x = 0$ .

- The wave functions fall off exponentially to zero as  $x \rightarrow \pm \infty$ . Hence the wave function  $\psi$  and the probability density  $|\psi|^2$  are not zero even for a large value of  $x$ . This is contrast to a classical harmonic oscillator which has a finite amplitude. The latter may be determined by equating the classical and quantum-mechanical energy expressions as given by Eqs (1.5.8) and (1.5.10), respectively, such that

$$\frac{1}{2} k_f A^2 = \left( v + \frac{1}{2} \right) h\nu_0, \quad \text{i.e.} \quad A = \left\{ \frac{(2v+1)h\nu_0}{k_f} \right\}^{1/2} \quad (1.5.13)$$

### Problem 1.5.1

#### Solution

- In the lowest vibrational level, the probability of finding the particle is maximum at the zero-displacement position (the so-called equilibrium position) and it decreases sharply as the displacement from the equilibrium position increased. In other words, it can be stated that the particle spends much of its time at the equilibrium position and the time spent at other positions becomes less and less as  $x$  is increased. This fact is in contradiction with the classical picture where the particle spends maximum time at the two extremes vibration and minimum time at the equilibrium position.

- On increasing the value of quantum number  $v$ , the maxima in the probability density curve are shifted towards the two extremes of the vibration. At very high quantum numbers, the probability density curve has two very large maxima very near to the two extremes and the rest of the maxima have smaller values. This means that only in the limit of very high quantum numbers, the particle spends much of its time at the two extremes—a behaviour which was predicted by the classical theory. This fact is in agreement with the correspondence principle which states that the classical behaviour emerges when high quantum numbers are reached.

Evaluate the expectation value of kinetic energy of the harmonic oscillator in the ground state.

The ground-state normalized wave function for the harmonic oscillator is

$$\psi_0 = \left( \frac{\sqrt{\alpha}}{\pi^{1/2}} \right)^{1/2} \exp(-\alpha x^2/2)$$

Since  $\psi_0$  is normalized the expectation value of kinetic energy is given by

$$\langle T \rangle = \int_{-\infty}^{+\infty} \psi_0 T_{op} \psi_0 dx$$

$$\text{Hence } \langle T \rangle = \int_{-\infty}^{+\infty} \left( \frac{\sqrt{\alpha}}{\pi^{1/2}} \right)^{1/2} \exp(-\alpha x^2/2) \left\{ \left( -\frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2} \right) \left( \frac{\sqrt{\alpha}}{\pi^{1/2}} \right)^{1/2} \exp(-\alpha x^2/2) \right\} dx$$

$$= \left( \frac{\sqrt{\alpha}}{\pi^{1/2}} \right)^2 \left( -\frac{h^2}{8\pi^2 m} \right) \int_{-\infty}^{+\infty} \exp(-\alpha x^2/2) \left\{ \frac{d^2}{dx^2} \exp(-\alpha x^2/2) \right\} dx$$

$$= \left( \frac{\sqrt{\alpha}}{\pi^{1/2}} \right)^2 \left( -\frac{h^2}{8\pi^2 m} \right) \left[ -\alpha \int_{-\infty}^{+\infty} \exp(-\alpha x^2) dx + \alpha^2 \int_{-\infty}^{+\infty} x^2 \exp(-\alpha x^2) dx \right]$$

$$= \left( \frac{\sqrt{\alpha}}{\pi^{1/2}} \right)^2 \left( -\frac{h^2}{8\pi^2 m} \right) \left[ -(\pi\alpha)^{1/2} + \frac{1}{2}(\pi\alpha)^{1/2} \right]$$

$$= \frac{\alpha h^2}{16\pi^2 m}$$

Since  $\alpha = 2\pi m\omega/h$ , and  $\omega = \sqrt{k_f/m}$ , we get

$$\langle T \rangle = \left( \frac{2\pi m\omega}{h} \right) \left( \frac{h^2}{16\pi^2 m} \right) = \frac{h\omega}{8\pi} = \frac{h}{8\pi} \sqrt{\frac{k_f}{m}} = \frac{h}{4} v_0$$

### Problem 1.5.2

Evaluate the expectation value of potential energy of the harmonic oscillator in the ground state and show that it has the same value as that of kinetic energy.

**Solution**

We have

$$\begin{aligned} \langle V \rangle &= \int \psi_0 V_{op} \psi_0 d\tau \\ &= \int_{-\infty}^{+\infty} \left( \frac{\sqrt{\alpha}}{\pi^{1/2}} \right)^{1/2} \exp(-\alpha x^2/2) \left( \frac{1}{2} k_f x^2 \right) \left( \frac{\sqrt{\alpha}}{\pi^{1/2}} \right)^{1/2} \exp(-\alpha x^2/2) dx \\ &= \left( \frac{\sqrt{\alpha}}{\pi^{1/2}} \right) \left( \frac{k_f}{2} \right) \int_{-\infty}^{+\infty} x^2 \exp(-\alpha x^2) dx \\ &= \left( \frac{\sqrt{\alpha}}{\pi^{1/2}} \right)^{1/2} \left( \frac{k_f}{2} \right) \left( \frac{\pi^{1/2}}{2\alpha^{3/2}} \right) \\ &= \frac{k_f}{4\alpha} = \left( \frac{k_f}{4} \right) \left( \frac{h}{2\pi m\omega} \right) = \frac{hk_f}{8\pi m} \sqrt{\frac{m}{k_f}} = \frac{h}{8\pi} \sqrt{\frac{k_f}{m}} = \frac{h}{4} v_0 \end{aligned}$$

On comparing  $\langle T \rangle$  and  $\langle V \rangle$ , we find that they are identical.

### Problem 1.5.3

Determine the value of  $x$  at which the ground-state wave function of the harmonic oscillator exhibits the maximum.

The ground-state wave function is

$$\psi_0 = \left( \frac{\sqrt{\alpha}}{\pi^{1/2}} \right)^{1/2} \exp(-\alpha x^2/2)$$

Making use of the mathematical criterion of maximum (i.e.  $d\psi_0/dx = 0$ ), we get

$$\frac{d\psi_0}{dx} = \left( \frac{\sqrt{\alpha}}{\pi^{1/2}} \right)^{1/2} \{-\alpha x \exp(-\alpha x^2/2)\} = 0$$

The above expression gives  $x = 0$  and  $x = \pm \infty$ .

To find the point of maximum, we evaluate the value of  $d^2\psi_0/dx^2$ , which gives

$$\frac{d^2\psi_0}{dx^2} = \left( \frac{\sqrt{\alpha}}{\pi^{1/2}} \right)^{1/2} [-\alpha + (\alpha x)^2] \exp(-\alpha x^2/2)$$

Obviously,  $d^2\psi_0/dx^2$  is negative at  $x = 0$ . Hence, the function  $\psi_0$  exhibits a maximum at  $x = 0$ .

### Problem 1.5.4

Determine the value of  $x$  at which the first excited wave function of the harmonic oscillator exhibits maximum (or minimum). Further, show that this value of  $x$  is 0.577 of the maximum displacement in the first excited state.

**Solution**

We have

$$\psi_1 = \left( \frac{\sqrt{\alpha}}{2\pi^{1/2}} \right)^{1/2} (2\sqrt{\alpha} x) \exp(-\alpha x^2/2)$$

$$\text{Now } \frac{d\psi_1}{dx} = \left( \frac{\sqrt{\alpha}}{2\pi^{1/2}} \right)^{1/2} \{ \exp(-\alpha x^2/2) - \alpha x \exp(-\alpha x^2/2) \} = 0$$

$$= \left( \frac{\sqrt{\alpha}}{2\pi^{1/2}} \right)^{1/2} (1 - \alpha x^2) \exp(-\alpha x^2/2) = 0$$

The roots at which the function  $\psi_1$  will exhibit a maximum and a minimum (or vice versa) are  $x = 1/\sqrt{\alpha}$  and  $x = -1/\sqrt{\alpha}$ , respectively.

Since  $\alpha = 2\pi m\omega/h$  and  $\omega = \sqrt{k_f/m}$ , we get

$$x = \pm \frac{1}{\sqrt{\alpha}} = \pm \left( \frac{h}{2\pi m\omega} \right)^{1/2} = \pm \left( \frac{h}{2\pi m} \sqrt{\frac{m}{k_f}} \right)^{1/2} = \pm \left( \frac{h}{2\pi} \sqrt{\frac{1}{k_f m}} \right)^{1/2}$$

The maximum displacement of the oscillator in the first excited state may be obtained by equating classical and quantum mechanical energy expressions. Thus, we have

$$\frac{1}{2} k_f x_{\max}^2 = \left( v + \frac{1}{2} \right) \frac{h}{2\pi} \sqrt{\frac{k_f}{m}}$$

Since for the first excited state,  $v = 1$ , we have

$$\frac{1}{2} k_f x_{\max}^2 = \frac{3}{2} \frac{h}{2\pi} \sqrt{\frac{k_f}{m}}$$

$$\text{or } x_{\max} = \left( 3 \frac{h}{2\pi} \sqrt{\frac{1}{k_f m}} \right)^{1/2} = 1.732 \left( \frac{h}{2\pi} \sqrt{\frac{1}{k_f m}} \right)^{1/2}$$

Thus  $x_{\max} = 1.732 x$

$$x = \frac{1}{1.732} x_{\max} = 0.577 x_{\max}$$

Evaluate the expectation values of  $x$ ,  $x^2$ ,  $p$  and  $p^2$  for the ground state of the harmonic oscillator and show that the product of root mean square uncertainties in  $p$  and  $x$  is in agreement with the uncertainty principle.

The normalized ground-state wave function for a harmonic oscillator is

$$\psi = \left( \frac{\sqrt{\alpha}}{\sqrt{\pi}} \right)^{1/2} \exp(-\alpha x^2/2)$$

Thus, we have

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi |x| \psi dx = \frac{\sqrt{\alpha}}{\sqrt{\pi}} \int_{-\infty}^{+\infty} x \exp(-\alpha x^2) dx$$

(since the integrand is odd)

$$\begin{aligned}\langle x^2 \rangle &= \int_{-\infty}^{+\infty} \psi |x|^2 \psi \, dx = \frac{\sqrt{\alpha}}{\sqrt{\pi}} \int_{-\infty}^{+\infty} x^2 \exp(-\alpha x^2) \, dx \\ &= \frac{\sqrt{\alpha}}{\sqrt{\pi}} \left\{ \frac{1}{2\alpha} \left( \frac{\pi}{\alpha} \right)^{1/2} \right\} = \frac{1}{2\alpha}\end{aligned}$$

$$\begin{aligned}\langle p \rangle &= \int_{-\infty}^{+\infty} \psi \left( \frac{h}{2\pi i} \frac{d}{dx} \right) \psi \, dx \\ &= \left( \frac{h}{2\pi i} \right) \left( \frac{\sqrt{\alpha}}{\sqrt{\pi}} \right) \int_{-\infty}^{+\infty} \exp(-\alpha x^2/2) \left\{ \frac{d}{dx} \exp(-\alpha x^2/2) \right\} dx \\ &= \left( \frac{h}{2\pi i} \right) \left( \frac{\sqrt{\alpha}}{\sqrt{\pi}} \right) (-\alpha) \int_{-\infty}^{+\infty} x \exp(-\alpha x^2/2) \, dx \\ &= 0 \quad (\text{since the integrand is odd})\end{aligned}$$

$$\begin{aligned}\langle p^2 \rangle &= \int_{-\infty}^{+\infty} \psi \left[ -\frac{h^2}{4\pi^2} \frac{d^2}{dx^2} \right] \psi \, dx \\ &= \left( -\frac{h^2}{4\pi^2} \right) \left( \frac{\sqrt{\alpha}}{\sqrt{\pi}} \right) \int_{-\infty}^{+\infty} \exp(-\alpha x^2/2) \frac{d^2}{dx^2} \left\{ \exp(-\alpha x^2/2) \right\} dx\end{aligned}$$

Carrying out the differentiation followed by integration by parts, we have

$$\begin{aligned}\langle p^2 \rangle &= \left( -\frac{h^2}{4\pi^2} \right) \left( \frac{\sqrt{\alpha}}{\sqrt{\pi}} \right) \left[ (-\alpha) \left( \frac{\pi}{\alpha} \right)^{1/2} + \alpha \left\{ \frac{1}{2\alpha^2} \left( \frac{\pi}{\alpha} \right)^{1/2} \right\} \right] \\ &= \left( -\frac{h^2}{4\pi^2} \right) \left( \frac{\sqrt{\alpha}}{\sqrt{\pi}} \right) \left( -\frac{\sqrt{\alpha}}{2} \sqrt{\pi} \right) = \frac{h^2 \alpha}{8\pi^2}\end{aligned}$$

$$\text{Now } \Delta x = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2} = \frac{1}{\sqrt{2\alpha}}$$

$$\Delta p = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2} = \frac{h\sqrt{\alpha}}{(2\sqrt{2\pi})}$$

$$\text{Thus } \Delta p \Delta x = \left( \frac{h\sqrt{\alpha}}{2\sqrt{2\pi}} \right) \left( \frac{1}{\sqrt{2\alpha}} \right) = \frac{h}{4\pi}$$

which is in agreement with the uncertainty principle.

**Problem 1.5.6** For the trial wave function  $\psi = a \exp(-bx^2)$  for a harmonic oscillator of mass  $m$ , show that the energy is given by

$$E = \frac{h^2 b}{8\pi^2 m} + \frac{k_t}{8b}$$

### Solution

Minimize  $E$  with respect to  $b$  and determine the expression for the minimum energy. Also determine the expression of  $a$  through normalization of wave function.

The Hamiltonian operator is

$$H_{op} = -\frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2} + \frac{1}{2} k_t x^2$$

The energy expression is

$$\begin{aligned}E &= \frac{\langle \psi | H_{op} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\langle a e^{-bx^2} | H_{op} | a e^{-bx^2} \rangle}{\langle a e^{-bx^2} | a e^{-bx^2} \rangle} \\ &= \frac{\langle e^{-bx^2} | \left[ -\frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2} + \frac{1}{2} k_t x^2 \right] e^{-bx^2} \rangle}{\langle e^{-2bx^2} \rangle} \\ &= \frac{\left\langle e^{-bx^2} \left| \left[ -\frac{h^2}{8\pi^2 m} (-2b + 4b^2 x^2) + \frac{1}{2} k_t x^2 \right] e^{-bx^2} \right| \right\rangle}{\langle e^{-2bx^2} \rangle} \\ &= \frac{h^2 b}{4\pi^2 m} + \left( -\frac{h^2 b^2}{2\pi^2 m} + \frac{1}{2} k_t \right) \left[ \int_{-\infty}^{+\infty} x^2 e^{-2bx^2} dx \right] \left/ \int_{-\infty}^{+\infty} e^{-2bx^2} dx \right. \\ &= \frac{h^2 b}{4\pi^2 m} + \left( -\frac{h^2 b^2}{2\pi^2 m} + \frac{1}{2} k_t \right) \left( \frac{\sqrt{\pi/2b}}{\sqrt{\pi/2b}} \right) = \frac{h^2 b}{8\pi^2 m} + \frac{k_t}{8b}\end{aligned}$$

To determine minimum energy, we set  $\partial E / \partial b = 0$ , which gives

$$\frac{h^2}{8\pi^2 m} - \frac{k_t}{8b^2} = 0 \Rightarrow b = \frac{\pi \sqrt{k_t m}}{h}$$

$$\begin{aligned}\text{Hence, } E_{\min} &= \frac{h^2}{8\pi^2 m} \left( \frac{\pi \sqrt{k_t m}}{h} \right) + \frac{k_t}{8} \left( \frac{h}{\pi \sqrt{k_t m}} \right) \\ &= \frac{h}{8\pi} \sqrt{\frac{k_t}{m}} + \frac{h}{8\pi} \sqrt{\frac{k_t}{m}} = \frac{h}{4\pi} \sqrt{\frac{k_t}{m}}\end{aligned}$$

The expression of normalization of wave function is

$$\int_{-\infty}^{+\infty} \psi^2 dx = 1$$

$$\text{i.e. } a^2 \int_{-\infty}^{+\infty} e^{-2bx^2} dx = 1 \Rightarrow a^2 \left( \frac{\pi}{2b} \right)^{1/2} = 1$$

$$\Rightarrow a = \left( \frac{2b}{\pi} \right)^{1/4} = \left( \frac{2}{\pi} \right)^{1/4} \left( \frac{\pi \sqrt{k_t m}}{h} \right)^{1/4} = \left( \frac{\sqrt{k_t m}}{h/2} \right)^{1/4}$$

The eigenfunction for the second excited state of a harmonic oscillator is given by

$$\psi_2 = N H_2 e^{-x^2/2} \text{ where } H_2 = 4y^2 - 2 = 4(\sqrt{\alpha} x)^2 - 2 = 2(2\alpha x^2 - 1)$$

$$\alpha = \frac{m\omega}{h/2\pi} = \frac{m\sqrt{k_t/m}}{h/2\pi} = \frac{2\pi m}{h} \sqrt{\frac{k_t}{m}} = \frac{4\pi^2 m}{h} \nu_0$$

**Solution**

- (a) Determine the normalization constant  $N$ . (b) Show that the energy of the oscillator is  $(5/2)h\nu_0$ .  
 (a) To determine the normalization constant, we set

$$\int_{-\infty}^{+\infty} \psi_2^2 dx = 1 \quad \text{i.e.} \quad \int_{-\infty}^{+\infty} 4N^2(2\alpha x^2 - 1)^2 e^{-\alpha x^2} dx = 1$$

$$\text{i.e.} \quad 4N^2 \left[ 4\alpha^2 \int_{-\infty}^{+\infty} x^4 e^{-\alpha x^2} dx + \int_{-\infty}^{+\infty} e^{-\alpha x^2} dx - 4\alpha \int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} dx \right] = 1$$

$$\text{i.e.} \quad 4N^2 \left[ 4\alpha^2 \left\{ 2 \cdot \frac{3}{8\alpha^2} \left( \frac{\pi}{\alpha} \right)^{1/2} \right\} + \left\{ 2 \cdot \frac{1}{2} \left( \frac{\pi}{\alpha} \right)^{1/2} \right\} - 4\alpha \left\{ 2 \cdot \frac{1}{4\alpha} \left( \frac{\pi}{\alpha} \right) \right\} \right] = 1$$

This gives  $N = \frac{1}{\sqrt{8}} \left( \frac{\alpha}{\pi} \right)^{1/4}$

- (b) Since  $\psi_2$  is an eigenfunction, we evaluate  $E_2$  by using the expression  $H_{op} \psi_2 = E_2 \psi_2$ . The Hamiltonian operator of the harmonic oscillator is

$$H_{op} = -\frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2} + \frac{1}{2} k_f x^2$$

The wavefunction  $\psi_2$  is

$$\psi_2 = \frac{2}{\sqrt{8}} \left( \frac{\alpha}{\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

We find what

$$\begin{aligned} \frac{d}{dx} (2\alpha x^2 - 1) e^{-\alpha x^2/2} &= [4\alpha x + (2\alpha x^2 - 1)(-\alpha x)] e^{-\alpha x^2/2} \\ &= (5\alpha x - 2\alpha^2 x^3) e^{-\alpha x^2/2} \\ \frac{d^2}{dx^2} (2\alpha x^2 - 1) e^{-\alpha x^2/2} &= \frac{d}{dx} (5\alpha x - 2\alpha^2 x^3) e^{-\alpha x^2/2} \\ &= [(5\alpha - 6\alpha^2 x^2) + (5\alpha x - 2\alpha^2 x^3)(-\alpha x)] e^{-\alpha x^2/2} \\ &= (5\alpha - 11\alpha^2 x^2 + 2\alpha^3 x^4) e^{-\alpha x^2/2} = (5\alpha - \alpha^2 x^2)(1 - 2\alpha^2 x^2) e^{-\alpha x^2/2} \end{aligned}$$

Hence,  $-\frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2} \psi_2 = -\frac{h^2}{8\pi^2 m} (-5\alpha + \alpha^2 x^2) \psi_2$

Now  $\frac{5h^2\alpha}{8\pi^2 m} = \frac{5h^2}{8\pi^2 m} \left( \frac{4\pi^2 m}{h} \nu_0 \right) = \frac{5}{2} h\nu_0$

$$\frac{h^2}{8\pi^2 m} (\alpha^2 x^2) = \frac{h^2}{8\pi^2 m} \left\{ \left( \frac{4\pi^2 m k_f}{h^2} \right) x^2 \right\} = \frac{1}{2} k_f x^2$$

With these

$$\begin{aligned} H_{op} \psi_2 &= \left( -\frac{h^2}{8\pi^2 m} \frac{d^2}{dx^2} + \frac{1}{2} k_f x^2 \right) \psi_2 \\ &= \left[ \left( \frac{5}{2} h\nu_0 - \frac{1}{2} k_f x^2 \right) + \frac{1}{2} k_f x^2 \right] \psi_2 = \left( \frac{5}{2} h\nu_0 \right) \psi_2 \end{aligned}$$

Thus  $E_2 = \left( \frac{5}{2} \right) h\nu_0$

## 1.6 QUANTIZATION OF ROTATIONAL ENERGY OF DIATOMIC MOLECULES

### Classical Treatment

While treating the rotational motion of a diatomic molecule, we can adopt a model of rigid rotator where the two masses  $m_1$  and  $m_2$  (representing the masses of the two atoms) are connected through a rigid rod of length  $r$  (equal to the distance between the two atoms of the molecule). Let this rigid rotator be rotated around an axis perpendicular to its own axis and passing through the centre of mass as shown in Fig. 1.6.1.

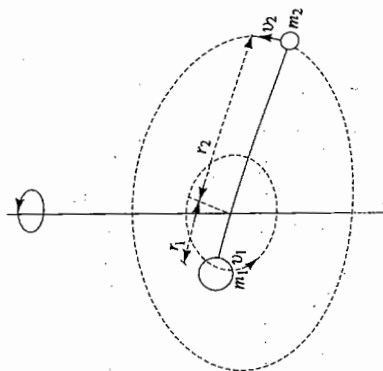


Fig. 1.6.1 The model of a rigid rotator

Let  $v_1$  and  $v_2$  be the respective velocities of the two particles with which they are rotating around the axis. The kinetic energy of the rotator is

$$T = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \quad (1.6.1)$$

For the two particles of rigid rotator, we have

$$v_1 = r_1 \omega$$

$$v_2 = r_2 \omega \quad (1.6.2)$$

where  $\omega$  is the angular velocity of the particles, and  $r_1$  and  $r_2$  are the respective distances of the two masses from the centre of mass of the molecule. Substitution of Eqs (1.6.2) and (1.6.3) in Eq. (1.6.1) gives

$$\begin{aligned} T &= \frac{1}{2} m_1 (r_1 \omega)^2 + \frac{1}{2} m_2 (r_2 \omega)^2 = \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) \omega^2 \\ &= \frac{1}{2} I \omega^2 \end{aligned} \quad (1.6.4)$$

where  $I$  is the moment of inertia of the system, by definition,

$$I = \sum_i m_i r_i^2$$

The moment of inertia  $I$  can be written in terms of the distance  $r$  between the two atoms. From the location of centre of mass, we have

$$m_1 r_1 = m_2 r_2 \quad (1.6.5)$$

Since  $r_1 + r_2 = r$ , we have

$$r_1 = \frac{m_2}{m_1 + m_2} r \quad \text{and} \quad r_2 = \frac{m_1}{m_1 + m_2} r \quad (1.6.6)$$

Substituting Eqs (1.6.6) in the expression

$$I = m_1 r_1^2 + m_2 r_2^2 \quad (1.6.7)$$

we get

$$I = m_1 \left( \frac{m_2}{m_1 + m_2} r \right)^2 + m_2 \left( \frac{m_1}{m_1 + m_2} r \right)^2 = \left( \frac{m_1 m_2}{m_1 + m_2} \right) r^2 = \mu r^2 \quad (1.6.8)$$

where  $\mu$  is the reduced mass of the system and is equal to  $m_1 m_2 / (m_1 + m_2)$ . Alternatively, it may be written as

$$\frac{1}{\mu} = \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \quad (1.6.9)$$

The kinetic energy expression  $T = (1/2) I \omega^2$  is the rotational counterpart of the kinetic energy expression  $T = (1/2) m v^2$  with  $I$  taking the place of  $m$  and  $\omega$  taking the place of  $v$ . Similar analogy between the linear momentum and the angular momentum gives

$$\text{Angular momentum, } L = I \omega \quad (1.6.10)$$

The kinetic energy of the system (Eq. 1.6.4) can be written in terms of angular momentum of the system:

$$T = \frac{1}{2} I \omega^2 = \frac{(I \omega)^2}{2I} = \frac{L^2}{2I} \quad (1.6.11)$$

Classically speaking, the kinetic energy of the rotator can have any value since  $\omega$  can possess any value. This is, however, not true in the framework of quantum mechanics. In the latter, it can be shown that the energies are quantized.

The classical kinetic energy of the rigid rotator can be written as

$$T = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} \quad (1.6.12)$$

where  $p_1$  and  $p_2$  are the linear momenta of the two particles of rigid rotator. For a rotator rotating freely, the potential energy is zero and hence its total energy is equal to its kinetic energy, i.e.

$$E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2}$$

$$\text{or} \quad E = \frac{p_x^2 + p_y^2 + p_z^2}{2m_1} + \frac{p_x^2 + p_y^2 + p_z^2}{2m_2} \quad (1.6.13)$$

where  $p_x, p_y$  and  $p_z$  are the three respective components of linear momentum along  $x, y$ - and  $z$ -axes perpendicular to each other. Replacing  $ps$  with the corresponding quantum mechanical operator, we get

### Schrödinger Equation in Terms of Internal Coordinates

It is convenient to express the rotation of a diatomic molecule in terms of the internal coordinates which are defined as

$$x = x_2 - x_1, \quad y = y_2 - y_1, \quad z = z_2 - z_1 \quad (1.6.15)$$

Now  $\frac{\partial^2}{\partial x_1^2} = \left( \frac{\partial}{\partial x_1} \right)^2 = \left\{ \frac{\partial x}{\partial x_1} \frac{\partial}{\partial x} \right\}^2 = \left\{ (-1) \frac{\partial}{\partial x} \right\}^2 = \frac{\partial^2}{\partial x^2}$

Similar expressions can be written for other differentials. Substituting these in Eq. (1.6.14), we get

$$\begin{aligned} H_{\text{op}} &= -\frac{h^2}{8\pi^2 m_1} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{h^2}{8\pi^2 m_2} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \\ &= -\frac{h^2}{8\pi^2} \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \\ &= -\frac{h^2}{8\pi^2 \mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \end{aligned} \quad (1.6.16)$$

Thus the Schrödinger equation for the rigid rotator is given by

$$-\frac{h^2}{8\pi^2 \mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi = E \psi \quad (1.6.17)$$

It is convenient to transform the above equation into spherical coordinates with  $m_1$  at the centre and  $m_2$  at the position  $r, \theta$  and  $\phi$  (Fig. 1.6.2a). The transformation equations are

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned}$$

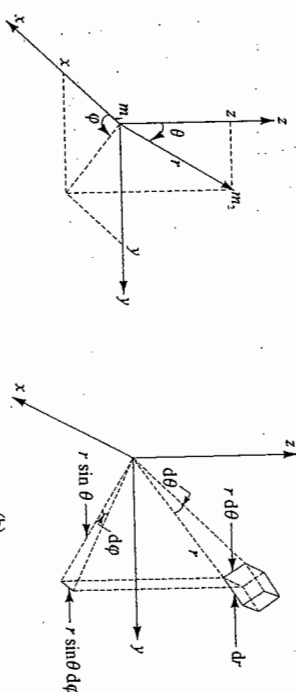


Fig. 1.6.2 (a) Cartesian and spherical coordinates, (b) volume element

Range of  $r$  is from 0 to  $\infty$   
Range of  $\theta$  is from 0 to  $\pi$   
Range of  $\phi$  is from 0 to  $2\pi$

$$\begin{aligned} dr &= (r \cdot d\theta) (r \sin \theta d\phi) \\ &= (r^2 d\theta) (\sin \theta d\phi) \end{aligned}$$

The transformed expression is given below.<sup>†</sup>

$$-\frac{\hbar^2}{8\pi^2\mu} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi = E\psi \quad (1.6.18)$$

Since the distance  $r$  between the two masses of the rotator remains constant, the derivative with respect to  $r$  will not appear in Eq. (1.6.18). Thus, Eq. (1.6.18) reduces to

$$-\frac{\hbar^2}{8\pi^2\mu r^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = EY(\theta, \phi) \quad (1.6.19)$$

where the function  $\psi$  has been replaced by a function by  $Y(\theta, \phi)$ , known as *spherical harmonics*, which depends only on the coordinates  $\theta$  and  $\phi$ . Equation (1.6.19) can be written as

$$\left[ -\frac{\hbar^2}{4\pi^2} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} \right] Y = (2EI)Y \quad (1.6.20)$$

Now according to Eq. (1.6.11), we have

$$2EI = L^2 \quad (1.6.21)$$

and moreover, the operation on the left side of Eq. (1.6.20) represents the operator of square of angular momentum<sup>‡</sup>. Hence, Eq. (1.6.20) may be written as

$$\hat{L}^2 Y = L^2 Y \quad (1.6.22)^{††}$$

The solution of Eq. (1.6.22) provides the following expression for the quantized values of  $L^2$ .

$$L^2 = J(J+1)(\hbar/2\pi)^2 \quad (1.6.23)$$

where  $J$  is the quantum number. The corresponding expression for the energy will be

$$E = \frac{L^2}{2I} = J(J+1) \frac{1}{2I} \left( \frac{\hbar}{2\pi} \right)^2 \quad (1.6.24)$$

Substituting Eq. (1.6.23) in Eq. (1.6.20), we get

$$\left[ -\frac{\hbar^2}{4\pi^2} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\} \right] Y = J(J+1) \left( \frac{\hbar}{2\pi} \right)^2 Y \quad (1.6.25)$$

$$\text{or} \quad \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + J(J+1)Y = 0 \quad (1.6.25)$$

<sup>†</sup> See Annexure V at the end of the chapter for the transformation.

<sup>‡</sup> See Annexure III at the end of the chapter for the derivation of expression of  $L_{\text{op}}^2$ .

<sup>††</sup> See Annexure VIII for the ladder-operator method to determine the eigenvalues of  $\hat{L}^2$  and  $\hat{L}_z$  and to determine the expressions of a few spherical harmonics  $Y$ .

Multiplying throughout by  $\sin^2 \theta$ , we get

$$\sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + J(J+1)Y \sin^2 \theta + \frac{\partial^2 Y}{\partial \phi^2} = 0 \quad (1.6.26)$$

The operator in Eq. (1.6.26) is made up of two terms, one depending on the independent variable  $\theta$  and the other on the independent variable  $\phi$ . Guided by this, we define the function  $Y(\theta, \phi)$  as a product of two functions  $\Theta(\theta)$  and  $\Phi(\phi)$ . This leads Eq. (1.6.26) to

$$\Phi \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + J(J+1)\Theta \sin^2 \theta + \Theta \frac{d^2 \Phi}{d\phi^2} = 0 \quad (1.6.27)$$

[Note that each of the derivatives in Eq. (1.6.27) is the total derivative instead of the partial derivative, since in each term the function contains only that variable with respect to which the derivative is taken.]

Dividing throughout by  $\Theta\Phi$  and rearranging, we have

$$\frac{1}{\Theta} \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + J(J+1) \sin^2 \theta = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \quad (1.6.28)$$

Now the left side of Eq. (1.6.28) involves only  $\theta$  whereas the right side involves only  $\phi$ . These two terms will be equal only when both are equal to the same constant, say  $m^2$ . Thus, we have

$$\frac{1}{\Theta} \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + J(J+1) \sin^2 \theta = m^2 \quad (1.6.29)$$

$$\text{and} \quad -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m^2 \quad (1.6.30)$$

Equation (1.6.30) can be written as

$$\frac{d^2 \Phi}{d\phi^2} = -m^2 \Phi \quad (1.6.31)$$

The solution of this equation is

$$\Phi_m = A \exp(im\phi) \quad (1.6.32)$$

When the angle  $\phi$  is replaced by  $(\phi + 2\pi)$ , the same set of points in space obtained. So the boundary condition is

$$\Phi(\phi + 2\pi) = \Phi(\phi) \quad (1.6.3)$$

Hence  $A \exp\{im(\phi + 2\pi)\} = A \exp(im\phi)$

$$\text{or} \quad \exp\{im2\pi\} = 1 \quad (1.6.3)$$

Since  $\exp(2\pi im) = \cos(2\pi m) + i \sin(2\pi m)$ , Eq. (1.6.34) will be true only if the constant  $m$  has a value of zero or a positive or negative integer, i.e.

$$m = 0, \pm 1, \pm 2, \dots \quad (1.6.35)$$

**Normalization of the Function  $\phi_m$** 

The value of  $A$  in Eq. (1.6.32) can be determined by normalizing the function  $\phi_m$  such that

$$\int_0^{2\pi} \phi_m^* \phi_m d\phi = 1$$

$$\text{or } A^* A \int_0^{2\pi} \exp(-im\phi) \exp(im\phi) d\phi = 1$$

$$\text{or } |A|^2 (2\pi) = 1$$

$$\text{or } A = \frac{1}{\sqrt{2\pi}}$$

Thus, the solution of Eq. (1.6.31) is

$$\phi_m = \frac{1}{\sqrt{2\pi}} \exp(im\phi); \quad m = 0, \pm 1, \pm 2, \dots \quad (1.6.36)$$

A few normalized  $\phi_m$  functions are given in Table 1.6.1.

**Table 1.6.1 A Few Normalized  $\phi_m$  Functions**

$m$	$\phi_m$
0	$1/\sqrt{2\pi}$
+1	$(1/\sqrt{2\pi}) \exp(i\phi)$
-1	$(1/\sqrt{2\pi}) \exp(-i\phi)$
+2	$(1/\sqrt{2\pi}) \exp(2i\phi)$
-2	$(1/\sqrt{2\pi}) \exp(-2i\phi)$

**Solution of Eq. (1.6.29)**

Equation (1.6.29) can be written in a more familiar form by defining a variable  $\xi = \cos \theta$

$$\text{Thus } \frac{d}{d\theta} \cdot \frac{d\xi}{d\theta} = (-\sin \theta) \frac{d}{d\xi}$$

$$\sin^2 \theta = 1 - \cos^2 \theta = 1 - \xi^2$$

and the function  $\Theta(\theta) \equiv P(\xi)$ .

With the above relations, Eq. (1.6.29) modifies to

$$\frac{1}{P} \left[ -(1-\xi^2) \right] \frac{d}{d\xi} \left[ -(1-\xi^2) \frac{dP}{d\xi} \right] + J(J+1)(1-\xi^2) = m^2$$

Dividing by  $(1-\xi^2)/P$  and rearranging, we get

$$\frac{d}{d\xi} \left[ (1-\xi^2) \frac{dP}{d\xi} \right] + \left[ J(J+1) - \frac{m^2}{(1-\xi^2)} \right] P = 0$$

$$\text{or } (1-\xi^2) \frac{d^2 P}{d\xi^2} - 2\xi \frac{dP}{d\xi} + \left[ J(J+1) - \frac{m^2}{1-\xi^2} \right] P = 0 \quad (1.6.37)$$

Equation (1.6.37) is a differential equation called the *associated Legendre equation*. The solution of Eq. (1.6.37) has been determined by the power series method. The various solutions  $P(\xi)$  of this equation are in the form of polynomial series, each of which must be restricted to a finite number of terms if the solution is to remain finite everywhere. This condition ultimately leads to the requirement that  $J$  be restricted to non-negative integer values, i.e.

$$J = 0, 1, 2, 3, \dots \quad (1.6.38)$$

The solution  $P$  are the *associated Legendre polynomials*  $P_J^{(m)}$  of degree  $J$  and order  $m$  and are given by the relation

$$P_J = P_J^{(m)} = (1-\xi^2)^{m/2} \frac{d^m P_J}{d\xi^m} \quad (1.6.39)$$

where  $P_J$  is the *Legendre polynomial* whose form depends only on integer  $J$  and is given by

$$P_J = \frac{1}{2^J J!} \frac{d^J}{d\xi^J} (\xi^2 - 1)^J \quad (1.6.40)$$

Besides  $J$  being a positive integer, the solution  $P$  of the function  $\Theta$  also requires that the  $|m| \leq J$  if the functions are not to vanish. This follows immediately from the fact that the differential  $(d^{|m|} P_J / d\xi^{|m|})$  will become zero if  $m$  is greater than  $J$  (Eq. 1.6.40). Thus, the two quantum conditions are

$$J = 0, 1, 2, 3, \dots \quad (1.6.38)$$

$$m = 0, \pm 1, \pm 2, \pm 3, \dots, \pm J \quad (1.6.41)$$

Hence,  $m$  can have  $(2J+1)$  values for a given value of  $J$ .

Now the functions  $\Theta(\theta)$  are identical to the solutions of the associated Legendre polynomials, i.e. of Eq. (1.6.39). However, the functions as given by Eq. (1.6.39) are not normalized. On normalizing Eq. (1.6.39) through the expression

$$\int_0^\pi \Theta^* \Theta \sin \theta d\theta = 1,$$

$$\text{we get } \Theta_{J, |m|} = \left[ \frac{(2J+1)(J-|m|)!}{2(J+|m|)!} \right]^{1/2} P_J^{(m)} \quad (1.6.42)$$

The function  $\Theta$  depends on the values of two quantum numbers  $J$  and  $|m|$ . The exact form of the function  $\Theta_{J, |m|}$  for the given values of  $J$  and  $|m|$  can be determined from Eqs (1.6.42), (1.6.39) and (1.6.40).

Determine the form of the function  $\Theta$  for  $J = 2$  and  $m = 0$ .

The  $\Theta$  function as given by Eq. (1.6.42) is

$$\Theta_{2,0} = \left[ \frac{(2 \times 2 + 1)}{2} \cdot \frac{2!}{2!} \right]^{1/2} P_2^{(0)}$$



where  $P_2^{(0)}$  from Eq. (1.6.39) is given by

$$P_2^{(0)} = (1 - \xi^2)^0 \frac{d^0}{d\xi^0} P_2 = P_2$$

and  $P_2$  from Eq. (1.6.40) is given by

$$\begin{aligned} P_2 &= \frac{1}{2^2(2!)} \frac{d^2}{d\xi^2} (\xi^2 - 1)^2 = \frac{1}{2^2(2!)} \frac{d}{d\xi} [2\xi(\xi^2 - 1)2\xi] \\ &= \frac{1}{2^2(2!)} [2(2\xi)(2\xi) + 2(\xi^2 - 1)2] \\ &= \frac{1}{8} [12\xi^2 - 4] = \frac{3}{2} \xi^2 - \frac{1}{2} \end{aligned}$$

$$\text{Hence, } \Theta_{2,0} = \left(\frac{5}{2}\right)^{1/2} \left(\frac{3}{2}\xi^2 - \frac{1}{2}\right) = \left(\sqrt{\frac{2 \times 5}{2 \times 2}}\right) \left(\frac{1}{2}(3\xi^2 - 1)\right)$$

$$= \frac{\sqrt{10}}{4} (3\xi^2 - 1)$$

Since  $\xi = \cos \theta$ , we have

$$\Theta_{2,0} = \frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$$

### Expressions of a Few $\Theta_{J,|m|}$ Functions

Following the method given in Problem 1.6.1, the other functions with different values of  $J$  and  $m$  can be determined. Table 1.6.2 includes some of these functions.

Table 1.6.2 A Few Normalized  $\Theta_{J,|m|}$  Functions

$J$	$m$	$\Theta_{J,m}$
0	0	$\sqrt{2}/2$
1	0	$(\sqrt{6}/2) \cos \theta$
1	$\pm 1$	$(\sqrt{3}/2) \sin \theta$
2	0	$(\sqrt{10}/4) (3 \cos^2 \theta - 1)$
2	$\pm 1$	$(\sqrt{15}/2) \sin \theta \cos \theta$
2	$\pm 2$	$(\sqrt{15}/4) \sin^2 \theta$

From Eq. (1.6.23), we have

$$L^2 = J(J+1) \left(\frac{h}{2\pi}\right)^2$$

$$\text{or } L = \sqrt{J(J+1)} (h/2\pi)$$

### Physical Significance of the Constant $J$

### Physical Significance of the Constant $m$

The minimum allowed value of  $J$  is zero, for which  $L$  as well as  $E$  has a value of zero. In the present case, angular momentum  $L$  can have a precise value.

In order to understand the physical significance of the constant  $m$ , let the function  $(1/\sqrt{2\pi}) \exp(im\varphi)$  be operated by the operator of  $z$ -component of angular momentum. The operator in spherical coordinate system has the form

$$\hat{L}_z = \frac{h}{2\pi i} \frac{\partial}{\partial \varphi} \quad (1.6.43)^\dagger$$

Thus, we have

$$\begin{aligned} \hat{L}_z \left\{ \frac{1}{\sqrt{2\pi}} \exp(im\varphi) \right\} &= \frac{h}{2\pi i} \frac{\partial}{\partial \varphi} \left\{ \frac{1}{\sqrt{2\pi}} \exp(im\varphi) \right\} \\ &= m \frac{h}{2\pi} \left\{ \frac{1}{\sqrt{2\pi}} \exp(im\varphi) \right\} \end{aligned} \quad (1.6.44)$$

Equation (1.6.44) represents an eigenvalue problem, where the  $z$ -component of angular momentum has a precise value and is given by the relation

$$L_z = m \left( \frac{h}{2\pi} \right) \quad (1.6.45)$$

Hence, the constant  $m$  represents the quantization of the  $z$ -component of the angular momentum. According to Eq. (1.6.44), the permitted values of  $m$  are  $0, \pm 1, \pm 2, \dots$ . Thus, the precise values of the  $z$ -component of angular momentum (i.e. the orientation angle  $\theta$  of the angular momentum with the  $z$ -axis) are allowed. This does not violate the uncertainty principle as the angle  $\varphi$  is completely unspecified.

The relation between  $J$  and  $m$  can also be determined by considering the eigenvalues of the operators  $\hat{L}^2$  and  $\hat{L}_z$

$$\text{We have } \hat{L}_z \left\{ \frac{1}{\sqrt{2\pi}} \exp(im\varphi) \right\} = m \frac{h}{2\pi} \left\{ \frac{1}{\sqrt{2\pi}} \exp(im\varphi) \right\}$$

<sup>†</sup> See Annexure III at the end of the chapter for the derivation of expression of  $\hat{L}_z$ .

$$\text{Thus } \hat{L}_z^2 \left\{ \frac{1}{\sqrt{2\pi}} \exp(im\phi) \right\} = \hat{L}_z \left\{ m \frac{h}{2\pi} \frac{1}{\sqrt{2\pi}} \exp(im\phi) \right\}$$

$$= m^2 \left( \frac{h}{2\pi} \right)^2 \left\{ \frac{1}{\sqrt{2\pi}} \exp(im\phi) \right\} \quad (1.6.46)$$

that is, the square of the z-component of angular momentum is  $(mh/2\pi)^2$ . Since the angular momentum is a vector quantity, we can write

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

$$\text{or } L^2 - L_z^2 = L_x^2 + L_y^2$$

$$\text{or } [J(J+1) - m^2] \left( \frac{h}{2\pi} \right)^2 = L_x^2 + L_y^2 \quad (1.6.47)$$

The right side of Eq. (1.6.47) is a positive quantity as it consists of a sum of squares. It, therefore, follows that the left side of this equation should also be a positive quantity for which we must have

$$J(J+1) - m^2 \geq 0 \quad (1.6.48)$$

This condition will be fulfilled provided  $|m| \leq J$ .

Thus, the values of  $m$  are restricted to  $m = 0, \pm 1, \pm 2, \dots, \pm J$ , i.e.  $m$  can have  $(2J+1)$  values. All states with different values of  $m$  but the same value of  $J$  are degenerate (i.e. they have the same energy) as the energy of the system depends only on the quantum number  $J$ .

Since  $m$  is confined to the  $(2J+1)$  discrete values  $J, (J-1), \dots, -(J-1), -J$  for a given value of  $J$ , it implies that the orientations of the angular momentum vector of magnitude  $\sqrt{J(J+1)} (h/2\pi)$  in space is such that its component along the z-axis can have values of  $m(h/2\pi)$ , where  $m$  can take any value out of  $J, (J-1), \dots, -(J-1), -J$ . The angular momentum being a vector quantity can be shown by an arrow whose length is proportional to the magnitude of the angular momentum and which points in a direction perpendicular to the plane of rotation. Thus, the orientations of the angular momentum vector and also the corresponding orientation of the plane of rotation may take only a discrete range of values, as shown in Fig. 1.6.3 for  $J = 1$ . This leads to what is known as the *space quantization of angular momentum*. The angle  $\theta$  between the angular momentum vector and the z-axis is given by the relation

$$\sqrt{J(J+1)} \cos \theta = m \quad (1.6.49)$$

In Fig. 1.6.3, the orientations of angular momentum vectors labelled as (i) and (ii) are in the plane of paper. For  $m$  not equal to zero the angular momentum vector can also point out of the plane of paper making the same angle  $\theta$  with the z-axis. These orientations are shown under the labelling (iii). Thus, any vector on the conical surfaces will have a value of  $\sqrt{2}(h/2\pi)$  for the total angular

momentum and  $\pm (h/2\pi)$  for the z-component of angular momentum. The fact that the angular momentum may lie anywhere on the cone is in agreement with the uncertainty principle (angle  $\theta$  has a precise value but not the angle  $\phi$ ). In other words, the quantities  $L^2$  and  $L_z$  have precise values but not  $L_x$  and  $L_y$ †

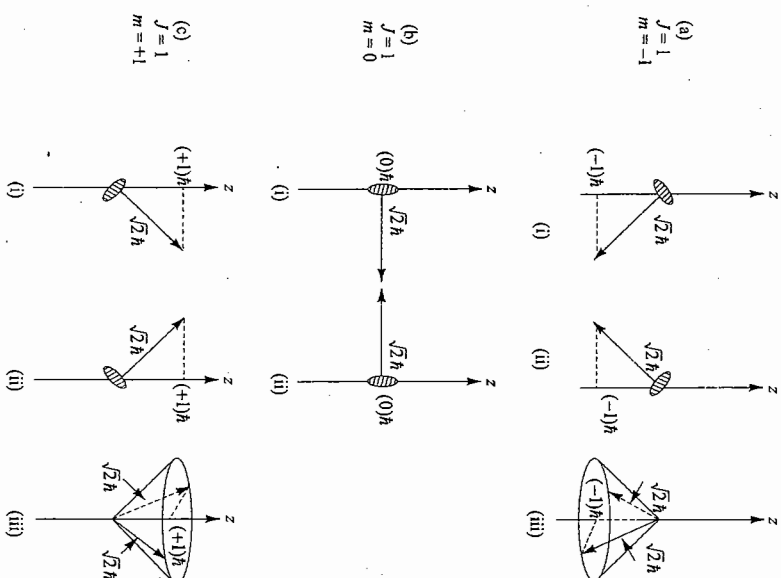


Fig. 1.6.3 Possible orientations of angular momentum vectors for  $J = 1$

### Problem 1.6.2

Show that  $\Theta_{2, \pm 11} \Phi_{+1}$  is an eigenfunction of

$$-\frac{\hbar^2}{4\pi^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

What is the eigenvalue? Given:  $\Theta_{2, \pm 11} = (\sqrt{15}/2) \sin \theta \cos \theta$  and  $\Phi_{+1} = (1/\sqrt{2\pi}) \exp(i\phi)$ .

We operate the given operator on the given wave function

$$-\frac{\hbar^2}{4\pi^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \Theta_{2, \pm 11} \Phi_{+1}$$

† See Annexure IV at the end of the chapter for quantum mechanical explanation.

$$\begin{aligned}
&= -\frac{h^2}{4\pi^2} \left[ \frac{\Phi_{+1}}{\sin \theta} \frac{d}{d\theta} \left( \frac{\sin \theta}{d\theta} \frac{d}{d\theta} \frac{\Phi_{2,1H}}{d\theta} \right) + \frac{\Phi_{2,1H}}{\sin^2 \theta} \frac{d^2}{d\theta^2} \Phi_{+1} \right] \\
&= \left( -\frac{h^2}{4\pi^2} \right) \left( \frac{\sqrt{15}}{2} \right) \left( \frac{1}{\sqrt{2\pi}} \right) \left[ \frac{e^{i\varphi}}{\sin \theta} \frac{d}{d\theta} \left( \frac{\sin \theta}{d\theta} \frac{d}{d\theta} \sin \theta \cos \theta \right) + \frac{\sin \theta \cos \theta}{\sin^2 \theta} \frac{d^2}{d\theta^2} e^{i\varphi} \right] \\
&= \left( -\frac{h^2}{4\pi^2} \right) \left( \frac{\sqrt{15}}{2} \right) \left( \frac{1}{\sqrt{2\pi}} \right) \left[ \frac{e^{i\varphi}}{\sin \theta} \frac{d}{d\theta} (\sin \theta \cos 2\theta) + \frac{\cos \theta}{\sin \theta} (-1) e^{i\varphi} \right] \\
&= \left( -\frac{h^2}{4\pi^2} \right) \left( \frac{\sqrt{15}}{2} \right) \left( \frac{e^{i\varphi}}{\sqrt{2\pi}} \right) \left( \frac{1}{\sin \theta} \right) [\sin \theta (-2 \sin 2\theta) + \cos \theta \cos 2\theta - \cos \theta] \\
&= \left( -\frac{h^2}{4\pi^2} \right) \left( \frac{\sqrt{15}}{2} \right) \left( \frac{e^{i\varphi}}{\sqrt{2\pi}} \right) \left( \frac{1}{\sin \theta} \right) [-4 \sin^2 \theta \cos \theta + \cos \theta (1 - 2 \sin^2 \theta) - \cos \theta] \\
&= \left( -\frac{h^2}{4\pi^2} \right) \left( \frac{\sqrt{15}}{2} \right) \left( \frac{e^{i\varphi}}{\sqrt{2\pi}} \right) \left( \frac{1}{\sin \theta} \right) (-6 \sin^2 \theta \cos \theta) \\
&= (6) \left( \frac{h^2}{4\pi^2} \right) \left( \frac{\sqrt{15}}{2} \right) \left( \frac{e^{i\varphi}}{\sqrt{2\pi}} \right) \sin \theta \cos \theta \left( \frac{e^{i\varphi}}{\sqrt{2\pi}} \right) = (6) \left( \frac{h^2}{4\pi^2} \right) \Phi_{2,1H} \Phi_{+1}
\end{aligned}$$

The eigenvalue is  $(6)(h^2/4\pi^2)$ , i.e.  $2(2+1)(h^2/2\pi^2)$ .

## 1.7 QUANTIZATION OF ELECTRONIC ENERGY: THE HYDROGEN ATOM

The mathematical framework of the Bohr's theory was based on the basic assumption of quantization of orbital angular momentum of the electron. It was seen earlier that this theory led to the quantization of electronic energies which formed the basis for explaining the experimental spectra of hydrogen-like species such as  $H$ ,  $He^+$ ,  $Li^{2+}$  and  $Be^{3+}$ . However, this theory was not entirely satisfactory as it failed to provide an interpretation of relative line intensities in the hydrogen spectrum and also failed completely when it was applied to explain the energies and spectra of more complex atoms. In this section, we consider the application of Schrödinger's wave theory to one-electron atom. In the subsequent section, it will be shown how the principles of this theory can be applied, in a more approximate way, to many-electron atoms.

The time-independent form of Schrödinger equation is

$$H_{op} \Psi_{total} = E_{total} \Psi_{total} \quad (1.7.1)$$

where  $H_{op}$  is the Hamiltonian operator,  $E_{total}$  is the total nonrelativistic energy and  $\Psi_{total}$  is the wave function for the total system. Since the hydrogen-like systems contain two particles, namely, nucleus and electron, it is obvious that the wave

function  $\Psi_{total}$  depends on the six coordinate variables, three for the electron ( $x_e, y_e, z_e$ ) and three for the nucleus ( $x_n, y_n, z_n$ ), both sets of coordinates refer to the common origin. The Hamiltonian operator consists of two terms, viz., the kinetic and potential energy terms. The kinetic energy operator will contain two terms, one for the electron and one for the nucleus. Thus, we have

$$\begin{aligned}
H_{op} &= T_{op} + V_{op} \\
&= \left( -\frac{h^2}{8\pi^2 m_e} \nabla_e^2 - \frac{h^2}{8\pi^2 m_n} \nabla_n^2 \right) - \frac{Ze^2}{(4\pi \epsilon_0) r} \quad (1.7.2)
\end{aligned}$$

All symbols have their usual meanings. Substituting Eq. (1.7.2) in Eq. (1.7.1), we have

$$\begin{aligned}
&\left[ -\frac{h^2}{8\pi^2 m_e} \left( \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right) - \frac{h^2}{8\pi^2 m_n} \left( \frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2} + \frac{\partial^2}{\partial z_n^2} \right) \right. \\
&\quad \left. - \frac{Ze^2}{(4\pi \epsilon_0) r} \right] \Psi_{total} = E_{total} \Psi_{total} \quad (1.7.3)
\end{aligned}$$

Equation (1.7.3) can be broken into two simpler equations, one involving the free movement of the centre of mass of the atom in space and the other involving the relative motion of the electron with respect to the nucleus within the atom.<sup>†</sup> The two equations are

$$-\frac{h^2}{8\pi^2 (m_e + m_n)} \left( \frac{\partial^2}{\partial x_c^2} + \frac{\partial^2}{\partial y_c^2} + \frac{\partial^2}{\partial z_c^2} \right) \psi_M = E_{trans} \psi_M \quad (1.7.4)$$

$$\text{and} \quad \left[ -\frac{h^2}{8\pi^2 \mu_e} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{(4\pi \epsilon_0) r} \right] \psi_e = E \psi_e \quad (1.7.5)$$

with  $E_{trans} + E = E_{total}$

Equation (1.7.4) is simply the Schrödinger equation for a free particle of mass  $(m_e + m_n)$ ,  $E_{trans}$  is the translational kinetic energy associated with the free movement of the centre of mass of the atom through space.

Equation (1.7.5) is the Schrödinger equation which represents the system in which an electron of reduced mass  $\mu$  is revolving around the stationary nucleus of positive charge  $Z$  at a distance of  $r$ . The behaviour of this electron can be described by the function  $\psi_e$  and  $E$  is the corresponding energy of the electron. The allowed values of electronic energies can be obtained by solving Eq. (1.7.5). Equation (1.7.4) which describes the motion of the centre of mass is of the same form as that of the particle in a three-dimensional box.

<sup>†</sup> See Annexure VI at the end of the chapter for explanation.

### Schrödinger Equation in Terms of Spherical Polar Coordinates

The solution of Schrödinger equation becomes very much simplified if the equation is expressed in the coordinate system that reflects the symmetry of the system. In the present case the potential energy field is spherical symmetry ( $V$  depends only on  $r$ ), and thus it is convenient to transform the Schrödinger equation (Eq. 1.7.5) into the spherical polar coordinates  $r$ ,  $\theta$  and  $\varphi$  (Fig. 1.6.2) by using the relations

$$\begin{aligned}x &= r \sin \theta \cos \varphi \\y &= r \sin \theta \sin \varphi \\z &= r \cos \theta\end{aligned}$$

The transformation (see Annexure V) is a lengthy and tedious process, and only the transformed expression is given below.

$$\left[ -\frac{\hbar^2}{8\pi^2\mu r^2} \left\{ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\} - \frac{Ze^2}{(4\pi\epsilon_0)r} \right] \psi = E\psi$$

where  $\psi$  is a function of  $r$ ,  $\theta$  and  $\varphi$ .

Rearranging the above expression, we get

$$\begin{aligned}\frac{1}{r^2} \left\{ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\} \psi \\ + \frac{8\pi^2\mu}{\hbar^2} \left( -\frac{Ze^2}{(4\pi\epsilon_0)r} + E \right) \psi = 0\end{aligned}$$

Multiplying throughout by  $r^2$  and rearranging the resultant expression, we get

$$\left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{8\pi^2\mu r^2}{\hbar^2} \left\{ -\frac{Ze^2}{(4\pi\epsilon_0)r} + E \right\} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \psi = 0 \quad (1.7.6)$$

Since the operator is made up of two terms, one depending on the variable  $r$  and the other on the variables  $\theta$  and  $\varphi$  taken together, we can write the wave function  $\psi$  as the product of two functions—one depending on  $r$  and the other on  $\theta$  and  $\varphi$ . Hence, we can write

$$\psi_{r,\theta,\varphi} = R_r Y_{\theta,\varphi} \quad (1.7.7)$$

The function  $Y$  is known as spherical harmonics. Substituting Eq. (1.7.7) in Eq. (1.7.6), we get

$$\begin{aligned}Y_{\theta,\varphi} \frac{d}{dr} \left( r^2 \frac{d}{dr} R_r \right) + \frac{8\pi^2\mu r^2}{\hbar^2} \left[ -\frac{Ze^2}{(4\pi\epsilon_0)r} + E \right] R_r Y_{\theta,\varphi} \\ + R_r \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] Y_{\theta,\varphi} = 0\end{aligned} \quad (1.7.8)$$

Dividing throughout by  $R_r Y_{\theta,\varphi}$ , we get

$$\begin{aligned}\left[ \frac{1}{R_r} \frac{d}{dr} \left( r^2 \frac{d}{dr} R_r \right) + \frac{8\pi^2\mu r^2}{\hbar^2} \left\{ -\frac{Ze^2}{(4\pi\epsilon_0)r} + E \right\} \right] \\ = - \left[ \frac{1}{Y_{\theta,\varphi}} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\} Y_{\theta,\varphi} \right]\end{aligned} \quad (1.7.9)$$

Equality shown in Eq. (1.7.9) holds good only when both sides are equal to a constant, say,  $l(l+1)$ . Thus Eq. (1.7.9) separates into two equations, one depending only on  $r$  and the other on  $\theta$  and  $\varphi$ . These are:

Equation involving the variable  $r$

$$\frac{1}{R_r} \frac{d}{dr} \left( r^2 \frac{dR_r}{dr} \right) + \frac{8\pi^2\mu r^2}{\hbar^2} \left( E + \frac{Ze^2}{(4\pi\epsilon_0)r} \right) = l(l+1) \quad (1.7.10)$$

Equation involving the angles  $\theta$  and  $\varphi$

$$\frac{1}{Y_{\theta,\varphi}} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\} Y_{\theta,\varphi} = -l(l+1) \quad (1.7.11)$$

Multiplying Eq. (1.7.11) by  $\sin^2 \theta$  and rearranging the resultant expression, we get

$$\left[ \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + l(l+1) \sin^2 \theta + \frac{\partial^2}{\partial \varphi^2} \right] Y_{\theta,\varphi} = 0 \quad (1.7.12)$$

Since the operator in Eq. (1.7.12) consists of two terms, one depending on  $\theta$  and the other on  $\varphi$ , we can write the wave function  $Y_{\theta,\varphi}$  as

$$Y_{\theta,\varphi} = \Theta_\theta \Phi_\varphi$$

With this, Eq. (1.7.12) becomes

$$\Phi_\varphi \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta_\theta}{d\theta} \right) + l(l+1) \sin^2 \theta \Theta_\theta \Phi_\varphi + \Theta_\theta \frac{d^2}{d\varphi^2} \Phi_\varphi = 0$$

Dividing throughout by  $\Theta_\theta \Phi_\varphi$  and rearranging, we get

$$\frac{\sin \theta}{\Theta_\theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta_\theta}{d\theta} \right) + l(l+1) \sin^2 \theta = - \frac{1}{\Phi_\varphi} \frac{d^2 \Phi_\varphi}{d\varphi^2} \quad (1.7.13)$$

The two sides of Eq. (1.7.13) must be equal to a constant, say  $m^2$ . Thus, we have

$$\frac{\sin \theta}{\Theta_\theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta_\theta}{d\theta} \right) + l(l+1) \sin^2 \theta = m^2 \quad (1.7.14)$$

and

$$\frac{1}{\Phi_\varphi} \frac{d^2 \Phi_\varphi}{d\varphi^2} = -m^2 \quad (1.7.15)$$

### Three Split Expressions of the Schrödinger Equation

Thus, the Schrödinger equation (1.7.6) for the hydrogen-like species can be separated into three equations. These are:

• Equation involving only  $r$

$$\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{8\pi^2 \mu r^2}{h^2} \left( E + \frac{Ze^2}{(4\pi\epsilon_0)r} \right) = l(l+1) \quad (\text{Eq. 1.7.10})$$

• Equation involving only  $\theta$

$$\frac{\sin \theta}{\theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\theta}{d\theta} \right) + l(l+1) \sin^2 \theta = m^2 \quad (\text{Eq. 1.7.14})$$

• Equation involving only  $\varphi$

$$\frac{1}{\varphi} \frac{d^2 \varphi}{d\varphi^2} = -m^2 \quad (\text{Eq. 1.7.15})$$

We now consider the acceptable solutions of Eqs (1.7.10), (1.7.14) and (1.7.15). Equation (1.7.15) has already been solved in connection with the rigid rotator system (Eq. 1.6.31). Its solution is

$$\varphi_m = \frac{1}{\sqrt{2\pi}} \exp(im\varphi); \quad m = 0, \pm 1, \pm 2, \dots \quad (\text{Eq. 1.6.36})$$

The constant  $m$  is called the *magnetic quantum number* and it represents the quantization of the  $z$ -component of the angular momentum since

$$\begin{aligned} \hat{L}_z \left\{ \frac{1}{\sqrt{2\pi}} \exp(im\varphi) \right\} &= \frac{h}{2\pi i} \frac{\partial}{\partial \varphi} \left\{ \frac{1}{\sqrt{2\pi}} \exp(im\varphi) \right\} \\ &= m \frac{h}{2\pi} \left\{ \frac{1}{\sqrt{2\pi}} \exp(im\varphi) \right\} \end{aligned} \quad (\text{Eq. 1.6.44})$$

Thus, the permitted values of  $z$ -component of the angular momentum of the electron are given by the expression  $m(h/2\pi)$ .

Equation (1.7.14) has also been solved in the rigid rotator system. The solution is

$$\Theta_{l,m} = \left[ \frac{(2l+1)}{2} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^{|m|} \quad (\text{Eq. 1.6.42})$$

where  $P_l^{|m|} = (1 - \xi^2)^{|m|/2} \frac{d^{|m|} P_l}{d\xi^{|m|}}$  : Associated Legendre polynomials (Eq. 1.6.39)

$P_l = \frac{1}{2^l l!} \frac{d^l}{d\xi^l} (\xi^2 - 1)^l$  : Legendre polynomials (Eq. 1.6.40)

and  $\xi = \cos \theta$

### Solutions of $r$ -Dependent Equation

$$\Delta^2 \Theta_{l,m} = l(l+1) \left( \frac{h}{2\pi} \right)^2 \Theta_{l,m} \quad (1.7.16)$$

With the help of a suitable transformation of independent variable and from the forms of solutions as the variable approaches zero and infinity, it is possible to write Eq. (1.7.10) in the following more familiar form, known as *associated Laguerre equation*.

$$\rho^2 \frac{d^2 L}{d\rho^2} + (j+1-\rho) \frac{dL}{d\rho} + (k-j)L = 0 \quad (1.7.17)$$

where the function  $R$  is related to the function  $L$  through the following transformation scheme.

$$R(r) = s(\rho) = e^{-\rho/2} F(\rho) = e^{-\rho/2} \rho^j L(\rho) \quad (1.7.18)$$

The terms  $\rho, j$  and  $k$  are given by

$$\rho = 2\alpha r \quad (1.7.19)$$

$$j = 2l + 1 \quad (1.7.20)$$

$$k = \lambda + l \quad (1.7.21)$$

$$\text{where } \alpha^2 = -\frac{8\pi^2 \mu E}{h^2} \quad (1.7.22)$$

$$\lambda = \frac{4\pi^2 \mu Z e^2}{(4\pi\epsilon_0) h^2 \alpha} \quad (1.7.23)$$

The solution of Eq. (1.7.17), as determined by the power series method, is the *associated Laguerre polynomial* of degree  $(k-j)$  and order  $j$ , and is given by

$$L \equiv L_k^j = \frac{d^j}{d\rho^j} L_k \quad (1.7.24)$$

where  $L_k$ , the *Laguerre polynomial* of degree  $k$ , is given by

$$L_k = e^\rho \frac{d^k}{d\rho^k} (\rho^k e^{-\rho}) \quad (1.7.25)$$

In order that the associated Laguerre polynomial is the acceptable solution<sup>†</sup> of Eq. (1.7.17), the following quantum restriction has to be satisfied.

$$k = 1, 2, 3, \dots, \infty \quad (1.7.26)$$

<sup>†</sup>Acceptable solutions, as usual, means that the wave function  $L(\rho)$  should be a well-behaved function and should vanish as  $\rho \rightarrow \infty$ . The latter condition requires that the polynomial must be restricted to a finite number of terms.

This quantum restriction leads to the fact that  $\lambda$  which is equal to  $k - l$  (Eq. 1.7.21) must also be an integer. Let  $\lambda$  be written as  $n$ , so that

$$k = n + l \quad (1.7.27)$$

Thus, the function  $R$  as given by Eq. (1.7.18) is

$$R = \rho^l e^{-\rho/2} L_{n+l}^{2l+1} \quad (1.7.28)$$

Normalizing the above solution through the expression

$$\int_0^\infty R^* R r^2 dr = 1$$

$$\text{we get } R = - \left\{ \frac{2Z}{na_0} \right\}^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \rho^l e^{-\rho/2} L_{n+l}^{2l+1} \quad (1.7.29)$$

$$\text{where } \rho = (2a_0)r = 2 \left( \frac{4\pi^2 \mu Z e^2}{nh^2 (4\pi\epsilon_0)} \right) r = \left( \frac{2Z}{na_0} \right) r \quad (1.7.30)$$

$$\text{and } a_0 = \frac{h^2 (4\pi\epsilon_0)}{4\pi^2 \mu e^2} \quad (1.7.31)$$

**Allowed Values of  $n$  and its Relation with  $l$**   
The constant  $n$  is referred to as the *principal quantum number*. If the associated Laguerre polynomial (Eq. 1.7.24) is not to vanish, we must have

$$j \leq k \quad (1.7.32)$$

Since  $j = 2l + 1$  and  $k = n + l$ , we have

$$(2l + 1) \leq (n + l) \quad (1.7.33)$$

or  $l + 1 \leq n$  or  $l \leq n - 1$

Since the allowed values of  $l$  are 0, 1, 2, 3, ..., it is obvious that the principal quantum number  $n$  cannot have a zero value. The allowed values of  $n$  are only positive integers. Thus, we have

$$n = 1, 2, 3, 4, \dots$$

$$l = 0, 1, 2, 3, \dots, (n - 1) \quad (1.7.34)$$

**Expressions for the Function  $R_{n,l}$**   
The exact form of the function  $R_{n,l}(r)$  for the given values of  $n$  and  $l$  can be determined from Eqs (1.7.29), (1.7.24) and (1.7.25). These equations are

$$R_{n,l} = - \left\{ \frac{2Z}{na_0} \right\}^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \rho^l e^{-\rho/2} L_{n+l}^{2l+1} \quad (1.7.29)$$

$$L_{n+l}^{2l+1} = \frac{d^{2l+1}}{d\rho^{2l+1}} L_{n+l} \quad (1.7.24)$$

$$\text{and } L_{n+l} = e^\rho \frac{d^{n+l}}{d\rho^{n+l}} (\rho^{n+l} e^{-\rho}) \quad (1.7.25)$$

$$\text{where } \rho = \left( \frac{2Z}{na_0} \right) r$$

### Problem 1.7.1

#### Solution

Determine the form of function  $R$  for the values of  $n = 2$  and  $l = 0$ . Substituting the given values of  $n$  and  $l$  in Eq. (1.7.29), we get

$$R_{2,0} = - \left\{ \frac{2Z}{2a_0} \right\}^3 \frac{(2-0-1)!}{2 \times 2[(2+0)!]^3} \rho^0 e^{-\rho/2} L_2^1$$

where  $L_2^1$  as given by Eq. (1.7.24) is

$$L_2^1 = \frac{d}{d\rho} L_2$$

where  $L_2$  as given by Eq. (1.7.25) is

$$L_2 = e^\rho \frac{d^2}{d\rho^2} (\rho^2 e^{-\rho})$$

Now working in the reverse direction, we have

$$L_2 = e^\rho \frac{d}{d\rho} \left\{ \frac{d}{d\rho} (\rho^2 e^{-\rho}) \right\} = e^\rho \frac{d}{d\rho} (2\rho e^{-\rho} - \rho^2 e^{-\rho})$$

$$= e^\rho (2e^{-\rho} - 2\rho e^{-\rho} - 2\rho e^{-\rho} + \rho^2 e^{-\rho})$$

$$= (2 - 4\rho + \rho^2)$$

$$L_2^1 = \frac{d}{d\rho} L_2 = \frac{d}{d\rho} (2 - 4\rho + \rho^2) = -4 + 2\rho$$

Finally, since  $\rho = \left( \frac{2Z}{na_0} \right) r = \left( \frac{Zr}{a_0} \right)$ , we have

$$R_{2,0} = - \left\{ \frac{Z}{2a_0} \right\}^3 \frac{1}{4 \times 8} \left\{ \frac{Z}{a_0} \right\} e^{-\rho/2} (-4 + 2\rho)$$

$$= \left( \frac{Z}{2a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$$

Following the method given in Problem 1.7.1, other functions with different values of  $n$  and  $l$  can be determined. Table 1.7.1 includes some such functions.

### Some of the $r$ -Dependent Solutions

Table 1.7.1 A Few Normalized  $R_{n,l}$  Functions

$n$	$l$	$R_{n,l}$
1	0	$2 \left( \frac{Z}{a_0} \right)^{3/2} \exp(-Zr/a_0)$
2	0	$\left( \frac{Z}{2a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) \exp(-Zr/2a_0)$
2	1	$\frac{1}{\sqrt{3}} \left( \frac{Z}{2a_0} \right)^{3/2} \left( \frac{Zr}{a_0} \right) \exp(-Zr/2a_0)$
3	0	$\frac{2}{3} \left( \frac{Z}{3a_0} \right)^{3/2} \left( 3 - \frac{2Zr}{a_0} + \frac{2Z^2 r^2}{9a_0^2} \right) \exp(-Zr/3a_0)$
3	1	$\frac{2\sqrt{2}}{9} \left( \frac{Z}{3a_0} \right)^{3/2} \left( \frac{2Zr}{a_0} - \frac{Z^2 r^2}{3a_0^2} \right) \exp(-Zr/3a_0)$
3	2	$\frac{4}{27\sqrt{10}} \left( \frac{Z}{3a_0} \right)^{3/2} \left( \frac{Z^2 r^2}{a_0^2} \right) \exp(-Zr/3a_0)$

where  $a_0 = \frac{h^2(4\pi\epsilon_0)}{4\pi^2\mu e^2}$

### Energy of the Electron

The allowed values of energy of the electron can be obtained from Eqs (1.7.22) and (1.7.23). From Eq. (1.7.23) we get

$$\alpha = \frac{4\pi^2\mu Ze^2}{(4\pi\epsilon_0)nh^2} \quad (\text{since } \lambda = n)$$

Substituting this in Eq. (1.7.22), we get

$$\left[ \frac{4\pi^2\mu Ze^2}{(4\pi\epsilon_0)nh^2} \right]^2 = - \frac{8\pi^2\mu E}{h^2}$$

Cancelling the common terms, we get

$$E = - \frac{1}{n^2} \left( \frac{2\pi^2\mu Z^2 e^4}{h^2(4\pi\epsilon_0)^2} \right) \quad (1.7.35)$$

Equation (1.7.35) is identical with the expression derived earlier from the Bohr's theory. Thus, the energy of the electron depends on the value of the principal quantum number  $n$  and is independent of the values of  $l$  and  $m$ . Since the quantum number  $n$  appears only in the function  $R(r)$ , we conclude that the energy depends only on the distance of the electron from the nucleus and not on its angular dependence.

### A Summary of the Quantum Mechanical Treatment of the Hydrogen-like Species

- To describe the quantum mechanical state of the hydrogen-like species, we need a function  $\psi$  which depends on the six independent variables, viz., three coordinates of the nucleus and three for the electron.

- If the function  $\Psi$  is written as

$$\Psi = \psi_M \psi_e$$

where  $\psi_M$  depends on the coordinates of the centre of mass and  $\psi_e$  on the internal coordinates, the Schrödinger equation separates into two independent equations; one for the motion of the atom as a whole and the other involving the internal coordinates of the atom. The latter one is of interest to us as it would give us the wave functions of the electron and the associated energies.

- The Schrödinger equation involving the internal coordinates is then transformed into the spherical polar coordinates.

- The Schrödinger equation splits into three equations if we write  $\psi_e$  as

$$\psi_e = R \Theta \Phi$$

The function  $R$  involves only  $r$ ,  $\Theta$  involves only the angle  $\theta$  and  $\Phi$  involves only angle  $\phi$ . The three resultant equations can be solved for the functions  $R$ ,  $\Theta$  and  $\Phi$  by suitable transformations. In order that these functions are finite, well-behaved and consistent with the boundary conditions, certain quantum restrictions are introduced. These restrictions appear in the form of quantum numbers.

- The functions  $R$  depend only on  $r$ , therefore, they describe the distribution of the electron as a function of  $r$  from the nucleus. These functions depend upon two quantum numbers,  $n$  and  $l$ . The permitted values of these numbers are:

$$n = 1, 2, 3, 4, \dots$$

$$l = 0, 1, 2, \dots, (n-1)$$

Principal quantum number:

Azimuthal quantum number:

We have different  $R$  functions for different values of  $n$  and  $l$ .

- The functions  $\Theta$  depend only on angle  $\theta$ , therefore, they describe the distribution as a function of angle  $\theta$ . These functions again, depend upon two quantum numbers, viz.,  $l$  and  $m$ . Though the permitted values of  $m$  are  $0, \pm 1, \pm 2, \dots, \pm l$ , the  $\Theta$  functions depend only on the magnitude of  $m$ , i.e.  $|m|$ .
- The functions  $\Phi$  depend only on angle  $\phi$ , therefore, they describe the distribution as a function of angle  $\phi$ . These functions depend only on the value of  $m$ .
- The two functions  $\Theta$  and  $\Phi$  taken together give the angular distribution of the electron. Thus, the total wave function  $\psi_e$  which constitutes what is known as an orbital, depends on the quantum numbers  $n$ ,  $l$  and  $m$ , i.e. we have different  $\psi_e$  functions (or orbitals) for different values of  $n$ ,  $l$  and  $m$  and hence different behaviour of the electron in the atom.

- The physical significance of quantum numbers  $n$ ,  $l$  and  $m$  are as follows.

(a) The principal quantum number describes the energy of the electron in the hydrogen-like species and is given by the relation

$$E = -\frac{1}{n^2} \left[ \frac{2\pi^2 \mu Z^2 e^4}{h^2 (4\pi\epsilon_0)^2} \right] = -\frac{1}{n^2} \left[ \frac{Z^2 e^2}{2(4\pi\epsilon_0) a_0} \right]$$

where  $a_0 = (4\pi\epsilon_0) h^2 / 4\pi^2 \mu e^2$ .

(b) The azimuthal quantum number describes the total angular momentum of the electron through the expression†

$$L^2 = l(l+1) \left( \frac{h}{2\pi} \right)^2$$

It is customary to designate the values of  $l$  by letters as given below.

value of $l$ :	0	1	2	3	4	5
designation:	s	p	d	f	g	h

The letters s, p, d and f are derived from the spectroscopic terms; sharp, principal, diffuse, and fundamental, respectively.

(c) The magnetic quantum number describes the  $z$ -component of the angular momentum of the electron through the equation

$$L_z = m(h/2\pi)$$

- The energy of the electron depends only on the value of  $n$  and not at all on  $l$  and  $m$ . Thus, all  $\psi_n$  functions (or orbitals) with the same value of  $n$  but different values of  $l$  and  $m$  are degenerate, i.e. they have the same energy (Table 1.7.2). Thus, the degeneracy of orbitals for given value of  $n$  is equal to  $n^2$ .

**Table 1.7.2** Energies of Orbital in a Hydrogen-like Species

(i) $n = 1$	$l = 0$	$m = 0$	$E = -\frac{2\pi^2 \mu Z^2 e^4}{(4\pi\epsilon_0)^2 h^2}$
(ii) $n = 2$	$l = 0$	$m = 0$	$E = -\frac{1}{4} \left[ \frac{2\pi^2 \mu Z^2 e^4}{(4\pi\epsilon_0)^2 h^2} \right]$
	$l = 1$	$m = +1$	
		$m = 0$	
		$m = -1$	(Four-fold degenerate)
(iii) $n = 3$	$l = 0$	$m = 0$	
	$l = 1$	$m = +1$	
		$m = 0$	$E = -\frac{1}{9} \left[ \frac{2\pi^2 \mu Z^2 e^4}{(4\pi\epsilon_0)^2 h^2} \right]$
		$m = -1$	
	$l = 2$	$m = +2$	
		$m = +1$	
		$m = 0$	
		$m = -1$	(Nine-fold degenerate)
		$m = -2$	

† It can be noted that for all states in which  $l = 0$ , i.e. for all s orbitals, the orbital angular momentum has a zero value (this is not possible in the Bohr's theory). The orbital motion of the electron in s orbitals without angular momentum is difficult to visualize in classical terms.

## Spectra of Hydrogen-like Species

The spectra of atoms are obtained when the electron is transferred from one wave function (or the orbital) to another wave function. A more rigorous quantum-mechanical study of transition between quantum states (states with different values of  $n$ ,  $l$  and  $m$ ) indicates that certain restrictions in the change in the values of  $l$  and  $m$  must be satisfied. The transitions which do not follow these restrictions are forbidden, i.e. they are not observed. These restrictions are referred to as the *selection rules*. For hydrogen-like species, we have the following rules.

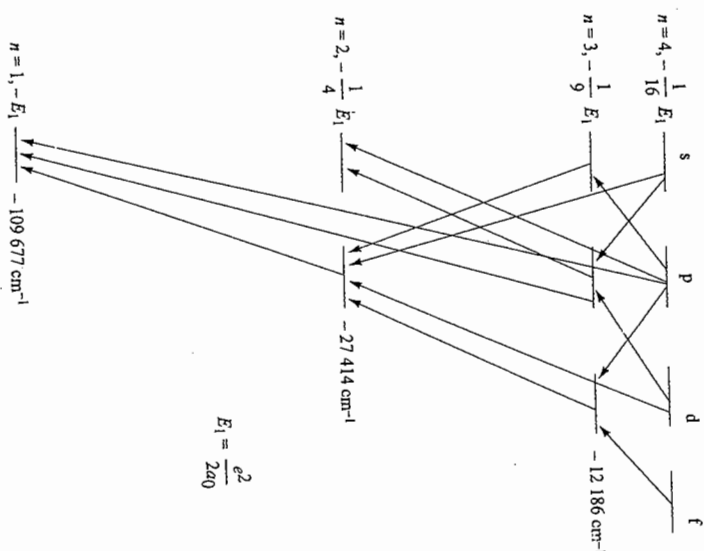
$n$  may change by an integer, i.e.  $\Delta n = \text{any value}$

$l$  must change by  $\pm 1$ , i.e.  $\Delta l = \pm 1$

and  $m$  may change by  $\pm 1$  or not at all i.e.  $\Delta m = 0, \pm 1$

For example, if an electron changes its principal quantum number from  $n = 2$  to  $n = 1$ , it must go from a state of  $l = 1$  to  $l = 0$ , i.e. the transition  $1s \leftarrow 2p$  is allowed. The transition  $1s \leftarrow 2s$  where  $\Delta l = 0$  is forbidden.

A few other possible transitions in the hydrogen atom are shown in Fig. 1.7.1. This diagram is known as Grotrian diagram. The fine structure of electronic spectrum due to spin-orbit coupling is described in Annexure IX at the end of this chapter.



**Fig. 1.7.1** The allowed transitions of the hydrogen atom



**Problem 1.7.2**

For the trial wave function  $\psi = \exp(-ar)$  for atomic hydrogen, show that the energy expression for the electron is

$$E = \frac{\hbar^2 a^2}{8\pi^2 m} - \frac{e^2 a_0}{4\pi\epsilon_0}$$

Minimize  $E$  with respect to  $a$ , solve for the constant  $a$  and find the expression for the minimum energy.

The Hamiltonian operator for atomic hydrogen is

$$H_{op} = -\frac{\hbar^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{(4\pi\epsilon_0)r}$$

The Laplacian operator  $\nabla^2$  in spherical polar coordinates is given by

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left( \frac{\partial^2}{\partial \phi^2} \right)$$

The expression of energy can be derived by using the expression

$$E = \frac{\langle \psi | H_{op} | \psi \rangle}{\langle \psi | \psi \rangle}$$

Since the given trial wave function is independent of angular coordinates, the expression of  $\nabla^2$  reduces to

$$\nabla^2 = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right)$$

$$\text{Thus } H_{op} \psi = \left( -\frac{\hbar^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{(4\pi\epsilon_0)r} \right) \psi$$

$$= -\frac{\hbar^2}{8\pi^2 m} \frac{1}{r^2} \frac{d}{dr} \left\{ r^2 \frac{d}{dr} \left( e^{-ar} \right) \right\} - \frac{e^2}{(4\pi\epsilon_0)r} e^{-ar}$$

$$= \left\{ -\frac{\hbar^2}{8\pi^2 m} \frac{1}{r^2} (-2ar + a^2 r^2) - \frac{e^2}{(4\pi\epsilon_0)r} \right\} e^{-ar}$$

$$\text{Now } \langle \psi | H_{op} | \psi \rangle = \int \psi | H_{op} | \psi \, d\tau \quad \text{where } d\tau = r^2 \, dr \, \sin \theta \, d\theta \, d\phi$$

Thus

$$\begin{aligned} \langle \psi | H_{op} | \psi \rangle &= \int_0^\infty \left\{ -\frac{\hbar^2}{8\pi^2 m} (-2ar + a^2 r^2) - \frac{e^2}{4\pi\epsilon_0} r \right\} e^{-2ar} dr \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} d\phi \\ &= \left[ -\frac{\hbar^2}{8\pi^2 m} \left\{ (-2a) \frac{1}{(2a)^2} + a^2 \frac{2}{(2a)^3} \right\} - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{2a} \right)^2 \right] (2)(2\pi) \\ &= \pi \left\{ \frac{\hbar^2}{8\pi^2 m} - \frac{e^2}{(4\pi\epsilon_0)a} \right\} \end{aligned}$$

**Solution**

$$\langle \psi | \psi \rangle = \int_0^\infty r^2 e^{-2ar} dr \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} d\phi = \frac{2}{(2a)^3} (2) (2\pi) = \frac{\pi}{a^3}$$

$$\begin{aligned} \text{Hence, } E &= \frac{\langle \psi | H_{op} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{(\pi/a) \left\{ (h^2/8\pi^2 m) - (e^2/4\pi\epsilon_0 a) \right\}}{(\pi/a^3)} \\ &= \frac{\hbar^2 a^2}{8\pi^2 m} - \left( \frac{e^2}{4\pi\epsilon_0} \right) a \end{aligned}$$

For minimizing  $E$  with respect to  $a$ , we set  $dE/da = 0$ , i.e.

$$\frac{\hbar^2}{8\pi^2 m} (2a) - \frac{e^2}{(4\pi\epsilon_0)} = 0$$

$$\text{which gives } a = \frac{4\pi^2 e^2 m}{\hbar^2 (4\pi\epsilon_0)}$$

$$\text{Hence } E_{\min} = \frac{\hbar^2}{8\pi^2 m} \left\{ \frac{4\pi^2 e^2 m}{\hbar^2 (4\pi\epsilon_0)} \right\}^2 - \frac{e^2}{4\pi\epsilon_0} \frac{4\pi^2 e^2 m}{\hbar^2 (4\pi\epsilon_0)} = -\frac{2\pi^2 e^4 m}{\hbar^2 (4\pi\epsilon_0)^2}$$

For the trial wave function  $\psi = \exp(-ar^2)$  for atomic hydrogen, show that the energy of electron is given by

$$E = \frac{3\hbar^2 a}{8\pi^2 m} - \frac{e^2 \sqrt{a}}{\sqrt{2}\epsilon_0 \pi^{3/2}}$$

Minimize  $E$  with respect to  $a$  and show that

$$E_{\min} = -\frac{e^4 m}{3\pi\epsilon_0^2 \hbar^2}$$

The Hamiltonian operator is

$$H_{op} = -\frac{\hbar^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{(4\pi\epsilon_0)r}$$

Since the given wave function does not include angular dependence, the expression of  $\nabla^2$  in spherical polar coordinates is

$$\nabla^2 = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right)$$

$$\begin{aligned} \text{Hence, } H_{op} \psi &= \left[ -\frac{\hbar^2}{8\pi^2 m} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) - \frac{e^2}{(4\pi\epsilon_0)r} \right] e^{-ar^2} \\ &= -\frac{\hbar^2}{8\pi^2 m} \frac{1}{r^2} \frac{d}{dr} (-2ar^3 e^{-ar^2}) - \frac{e^2}{(4\pi\epsilon_0)r} e^{-ar^2} \\ &= -\frac{\hbar^2}{8\pi^2 m} \frac{1}{r^2} (-6ar^2 + 4a^2 r^4) e^{-ar^2} - \frac{e^2}{(4\pi\epsilon_0)r} e^{-ar^2} \end{aligned}$$

**Solution**

$$\begin{aligned}\text{Thus } \langle \psi | H_{op} | \psi \rangle &= \int_0^\infty \left[ \frac{h^2}{8\pi^2 m} (6a - 4a^2 r^2) - \frac{e^2}{(4\pi\epsilon_0)r} \right] e^{-2ar^2} r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= \left[ \frac{h^2}{8\pi^2 m} \left\{ (6a) \int_0^\infty r^2 e^{-2ar^2} dr - (4a^2) \int_0^\infty r^4 e^{-2ar^2} dr \right\} \right. \\ &\quad \left. - \frac{e^2}{(4\pi\epsilon_0)} \int_0^\infty r e^{-2ar^2} dr \right] (2) (2\pi)\end{aligned}$$

$$\begin{aligned}&= \left[ \frac{h^2}{8\pi^2 m} \left\{ (6a) \frac{1}{4(2a)} \left( \frac{\pi}{2a} \right)^{1/2} - (4a^2) \frac{3}{8(2a)^2} \left( \frac{\pi}{2a} \right)^{1/2} \right\} \right. \\ &\quad \left. - \left( \frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{2} \left( \frac{1}{2a} \right) \right] (4\pi)\end{aligned}$$

$$= \frac{3h^2}{16\sqrt{2}m} \left( \frac{1}{\pi a} \right)^{1/2} - \left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{\pi}{a} \right)$$

$$\begin{aligned}\text{Also } \langle \psi | \psi \rangle &= \int_0^\infty r^2 e^{-2ar^2} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{1}{4(2a)} \left( \frac{\pi}{2a} \right)^{1/2} (4\pi) = \left( \frac{\pi}{2a} \right)^{3/2}\end{aligned}$$

$$\begin{aligned}\text{Hence } E &= \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\frac{3h^2}{16\sqrt{2}m} \left( \frac{1}{\pi a} \right)^{1/2} - \left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{\pi}{a} \right)}{\left( \frac{\pi}{2a} \right)^{3/2}} \\ &= \frac{3h^2 a}{8\pi^2 m} - (2\sqrt{2}) \left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{a}{\pi} \right)\end{aligned}$$

To minimize  $E$ , we set  $dE/da = 0$ , i.e.

$$\frac{3h^2}{8\pi^2 m} - (2\sqrt{2}) \left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{1}{\pi a} \right)^{1/2} = 0$$

This gives

$$a = \left[ \frac{\sqrt{2}(e^2/4\pi\epsilon_0)(1/\pi a)^{1/2}}{3h^2/8\pi^2 m} \right]^2 = \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \left( \frac{128\pi^3 m^2}{9h^4} \right)$$

The expression of minimum energy is given by

$$E = \left( \frac{3h^2}{8\pi^2 m} \right) \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \left( \frac{128\pi^3 m^2}{9h^4} \right) - 2 \left( \frac{2}{\pi} \right)^{1/2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{128\pi^3 m^2}{9h^4} \right)^{1/2}$$

### Problem 1.7.4

#### Solution

$$\begin{aligned}&= \frac{16\pi m}{3h^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 - \frac{2 \times 16\pi m}{3h^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \\ &= - \left( \frac{16\pi m}{3h^2} \right) \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 = - \frac{e^4 m}{3\pi\epsilon_0^2 h^2}\end{aligned}$$

Calculate the expectation value of  $r$  for an electron in the ground state of hydrogen atom ( $Z = 1$ ).

The ground state of hydrogen atom implies that  $n = 1$ ,  $l = 0$  and  $m = 0$ . The normalized wave function representing this state is

$$\psi_{1,0,0} = R_{1,0} \Theta_{0,0} \Phi_0$$

$$= \left[ 2 \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0} \right] \left[ \left( \frac{1}{\sqrt{2}} \right) \left( \frac{1}{\sqrt{2}\pi} \right) \right] \left[ \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \right]$$

For the normalized wave function  $\psi_{1,0,0}$ , the expectation value of  $r$  is given by

$$\langle r \rangle = \langle \psi_{1,0,0} | r | \psi_{1,0,0} \rangle$$

$$= \int \left[ \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \right] r \left[ \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \right] d\tau = \left( \frac{1}{\pi a_0^3} \right) \int r e^{-2r/a_0} d\tau$$

Since  $d\tau = r^2 dr \sin \theta d\theta d\phi$ , we get

$$\begin{aligned}\langle r \rangle &= \left( \frac{1}{\pi a_0^3} \right) \int_0^\infty r^3 e^{-2r/a_0} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= \left( \frac{1}{\pi a_0^3} \right) \left[ \frac{3!}{(2/a_0)^4} \right] (2)(2\pi) = \frac{3}{2} a_0\end{aligned}$$

Calculate the average distance of 2s electron from the nucleus of hydrogen atom.

The normalized wave function of 2s electron in hydrogen atom is

$$\psi_{2,0,0} = R_{2,0} \Theta_{0,0} \Phi_0$$

$$\begin{aligned}&= \left[ \left( \frac{1}{2a_0} \right)^{3/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0} \right] \left[ \left( \frac{1}{\sqrt{2}} \right) \left( \frac{1}{\sqrt{2}\pi} \right) \right] \\ &= \frac{1}{\sqrt{32}\pi} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0}\end{aligned}$$

The average value of  $r$  is given by

$$\begin{aligned}\langle r \rangle &= \langle \psi_{2,0,0} | r | \psi_{2,0,0} \rangle \\ &= \int \left[ \frac{1}{\sqrt{32}\pi} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0} \right] r \left[ \frac{1}{\sqrt{32}\pi} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0} \right] d\tau\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{32\pi} \left( \frac{1}{a_0^3} \right) \int_0^\infty r^2 \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \\
&= \frac{1}{32\pi} \left( \frac{1}{a_0^3} \right) \int_0^\infty r^3 \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \\
&= \frac{1}{32\pi} \left( \frac{1}{a_0^3} \right) \left[ \int_0^\infty \left( 4r^3 + \frac{r^5}{a_0} - \frac{4r^4}{a_0} \right) e^{-r/a_0} dr \right] (2) (2\pi) \\
&= \frac{1}{32\pi} \left( \frac{1}{a_0^3} \right) \left[ 4 \frac{3!}{(1/a_0)^4} + \frac{1}{a_0^2} \frac{5!}{(1/a_0)^6} - \frac{4}{a_0} \frac{4!}{(1/a_0)^5} \right] (4\pi) \\
&= \left( \frac{1}{32\pi} \right) \left( \frac{1}{a_0^3} \right) [(24 + 120 - 96) a_0^4] (4\pi) = \left( \frac{1}{32\pi} \right) \left( \frac{1}{a_0^3} \right) (48a_0^4) (4\pi) \\
&= 6a_0
\end{aligned}$$

**Note:** A 2s electron is much farther away from the nucleus as compared to 1s electron.

### Problem 1.7.6

Calculate the expectation value of potential energy,  $V$ , of electron in the ground state wave function of hydrogen atom. Also show that (i)  $\langle V \rangle = 2\langle E \rangle$ , (ii)  $\langle V \rangle = -2\langle T \rangle$ , and (iii)  $\langle T \rangle = -\langle E \rangle$ , where  $T$  stands for kinetic energy.

The ground state of hydrogen atom implies that  $n = 1$ ,  $l = 0$  and  $m = 0$ . The normalized wave function representing this state is

$$\psi_{1,0,0} = R_{1,0} \Theta_{0,0} \Phi_0 = \left[ 2 \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0} \right] \left( \frac{1}{\sqrt{2}} \right) \left( \frac{1}{\sqrt{2\pi}} \right) = \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0}$$

The expression of potential energy of electron in hydrogen atom is

$$V = -\frac{e^2}{(4\pi\epsilon_0)r}$$

For the normalized wave function  $\psi_{1,0,0}$ , the expectation value of potential energy is given by

$$\begin{aligned}
\langle V \rangle &= \langle \psi_{1,0,0} | V | \psi_{1,0,0} \rangle \\
&= \int \left[ \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \right] \left[ -\frac{e^2}{(4\pi\epsilon_0)r} \right] \left[ \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \right] d\tau \\
&= \left( \frac{1}{\pi a_0^3} \right) \left( -\frac{e^2}{4\pi\epsilon_0} \right) \int \frac{1}{r} e^{-2r/a_0} d\tau
\end{aligned}$$

Since  $d\tau = r^2 dr \sin \theta d\theta d\phi$ , we get

$$\begin{aligned}
\langle V \rangle &= \left( \frac{1}{\pi a_0^3} \right) \left( -\frac{e^2}{4\pi\epsilon_0} \right) \int_0^\infty r e^{-2r/a_0} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \\
&= \left( \frac{1}{\pi a_0^3} \right) \left( -\frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{1}{(2/a_0)^2} \right) (2) (2\pi) \\
&= -\frac{e^2}{(4\pi\epsilon_0)a_0}
\end{aligned}$$

Also, we have

(i) Since  $\langle E \rangle = -(e^2/4\pi\epsilon_0) (1/2a_0)$ , we find that

$$\langle V \rangle = 2\langle E \rangle$$

(ii) Since  $\langle E \rangle = \langle T \rangle + \langle V \rangle$ , we find that

$$\langle T \rangle = \langle E \rangle - \langle V \rangle = \frac{1}{2} \langle V \rangle - \langle V \rangle = -\frac{1}{2} \langle V \rangle$$

$$\text{or } \langle V \rangle = -2\langle T \rangle$$

(iii) Since  $\langle E \rangle = \langle T \rangle + \langle V \rangle$ , we find that

$$\langle T \rangle = \langle E \rangle - \langle V \rangle = \langle E \rangle - 2\langle E \rangle = -\langle E \rangle$$

**Note:** The expression  $\langle V \rangle = 2\langle E \rangle$  is known as the virial theorem. This expression is true for all systems involving only Coulombic potential energy.

### Problem 1.7.7

#### Solution

Calculate the most probable distance of the electron in 1s orbital of hydrogen atom.

To determine the most probable distance of the electron from the nucleus, we set  $d(r^2 R_{1,0}^2)/dr = 0$ . Taking the function  $R_{1,0}$  without constant factor, we get

$$\frac{d}{dr} (r^2 e^{-2r/a_0}) = 0$$

$$\text{i.e. } [2r + r^2(-2/a_0)] e^{-2r/a_0} = 0$$

This gives  $r = a_0$

### Problem 1.7.8

#### Solution

Calculate the most probable distance of the electron in 2s orbital of hydrogen atom. Also calculate the values of corresponding radial distribution function for the thickness  $a_0$  of the spherical shell.

To determine the most probable distance of the electron from the nucleus, we set  $d(r^2 R_{2,0}^2)dr = 0$ . Taking the function  $R_{2,0}$  without constant factor, we get

$$\frac{d}{dr} \left[ r^2 (2 - r/a_0)^2 e^{-r/a_0} \right] = 0$$

$$\text{i.e. } \frac{d}{dr} \left[ \left( 4r^2 + \frac{r^4}{2} - \frac{4r^3}{a_0} \right) e^{-r/a_0} \right] = 0$$

$$\text{i.e. } \left[ \left( 8r + \frac{4r^3}{a_0^2} - \frac{12r^2}{a_0} \right) + \left( 4r^2 + \frac{r^4}{a_0^2} - \frac{4r^3}{a_0} \right) \left( -\frac{1}{a_0} \right) \right] e^{-r/a_0} = 0$$

$$\text{i.e. } 8r + \frac{8r^3}{a_0^2} - \frac{16r^2}{a_0} - \frac{r^4}{a_0^3} = 0$$

This is equivalent to

$$\left( \frac{r}{a_0} \right)^3 - 8 \left( \frac{r}{a_0} \right)^2 + 16 \left( \frac{r}{a_0} \right) - 8 = 0$$

This expression is factored into

$$\left[ \left( \frac{r}{a_0} \right)^2 - 6 \left( \frac{r}{a_0} \right) + 4 \right] \left( \frac{r}{a_0} - 2 \right) = 0$$

The roots are

$$\frac{r}{a_0} = 2 \text{ and } \frac{r}{a_0} = \frac{6 \pm \sqrt{36 - 16}}{2} = 3 \pm \sqrt{5}$$

At  $r/a_0 = 2$ , we have node in the wave function  $R_{2,0}$ . There are two maxima in the plot of  $r^2 R^2$  versus  $r$  at  $r = (3 - \sqrt{5})a_0$  and  $(3 + \sqrt{5})a_0$ , respectively.

The radial distribution function for the spherical shell situated at a distance  $r$  from the nucleus is given by

$$F = r^2 R^2 dr$$

For 2s orbital, we have

$$\begin{aligned} F &= r^2 \left[ \left( \frac{1}{2a_0} \right)^{3/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0} \right]^2 dr \\ &= \left[ \frac{1}{8a_0} \left( \frac{r}{a_0} \right)^2 \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0} \right] dr \end{aligned}$$

For the thickness  $a_0$ , we have

$$F = \frac{1}{8} \left( \frac{r}{a_0} \right)^2 \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0}$$

For  $r/a_0 = 3 - \sqrt{5} = 0.764$ , we have

$$F = \frac{1}{8} (0.764)^2 (2 - 0.764)^2 e^{-0.764}$$

$$= \frac{1}{8} (0.584)(1.528)(0.466)$$

$$= 0.052$$

For  $r/a_0 = 3 + \sqrt{5} = 5.236$ , we have

$$F = \frac{1}{8} (5.236)^2 (2 - 5.236)^2 e^{-5.236}$$

$$= \frac{1}{8} (27.416)(10.472)(0.00532)$$

$$= 0.191$$

## 1.8 PICTORIAL REPRESENTATIONS OF WAVE FUNCTIONS AND PROBABILITY DENSITY DISTRIBUTIONS FOR HYDROGEN-LIKE SPECIES

### Expression of Wave Function

The various wave functions for the hydrogen-like species are written as

$$\psi_{n,l,m} = R_{n,l} \Theta_{l,m} \Phi_m$$

where the functions  $R_{n,l}$ ,  $\Theta_{l,m}$  and  $\Phi_m$  describe the  $r$ ,  $\theta$  and  $\varphi$  dependences, respectively. The function  $R$  depends on the two quantum numbers,  $n$  and  $l$ ;  $\Theta$  also depends on two quantum numbers,  $l$  and  $m$  and the function  $\Phi$  depends only on one quantum number  $m$ . The two functions  $\Theta_{l,m}$  and  $\Phi_m$  taken together describe the angular dependence of the wave function. A few  $R$ ,  $\Theta$  and  $\Phi$  functions have already been given in Tables 1.7.1, 1.6.2 and 1.6.1, respectively. At the very outset, two important features may be pointed out. These are:

1. The angular dependence depends on the quantum numbers  $l$  and  $m$  and not at all on the principal quantum number  $n$ . Thus, the angular dependence of the functions with different values of  $n$  but the same values of  $l$  and  $m$  is identical.
2. The angular part of the wave function for an s-orbital is a constant  $(1/4\pi)^{1/2}$  with no  $\theta$  and  $\varphi$  dependence for all values of  $n$ . Thus, the functions  $\psi_{1s}$ ,  $\psi_{2s}$ ,  $\psi_{3s}$ , ... (or simply 1s, 2s, 3s, ... orbitals) depend only on  $r$  and are spherically symmetrical.

Since for s-orbitals

$$\psi_{n,0,0} = \frac{1}{\sqrt{4\pi}} R_{n,0} \quad (1.8.1)$$

The plots of  $\psi_{n,0,0}$  versus  $r$  will have the same form as those of  $R$  versus  $r$ .

Plots of  $R_{1s}$  and  $R_{2s}$ 

Figure 1.8.1 shows the two-dimensional plots of functions  $R_{1s}$  and  $R_{2s}$  as a function of  $r$ .† In three dimensions the diagram will include the plots shown in Fig. 1.8.1 all around the nucleus.

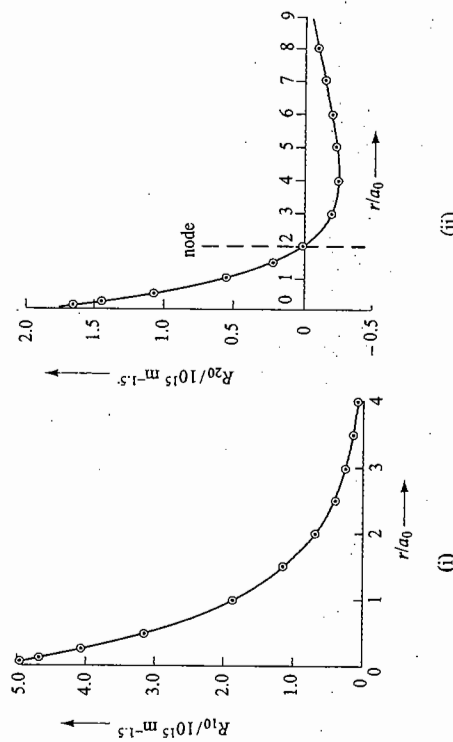


Fig. 1.8.1 Plots of functions (i)  $R_{1s}$  and (ii)  $R_{2s}$

The function  $\psi_{1s}$  simply shows the exponential decay with  $r$  as its form is  $2(Z/a_0)^{3/2} \exp(-Zr/a_0)$ .

The function  $\psi_{2s}$  is not as simple. It contains a constant term  $(Z/2a_0)^{3/2}$  and the term  $(2 - Zr/a_0) \exp(-Zr/2a_0)$ . The exponential factor of this function is just half of the corresponding exponential factor of the function  $\psi_{1s}$ , thus the value of  $\psi_{2s}$  decreases more slowly as compared to that of  $\psi_{1s}$ . Besides this, the factor  $(2 - Zr/a_0)$  introduces the new feature in the function  $\psi_{2s}$ . Depending upon the value of  $Zr/a_0$ , the function  $\psi_{2s}$  can be positive or zero or negative, i.e. if

$$\frac{Zr}{a_0} < 2, \quad \psi_{2s} \text{ is positive;} \quad \text{true for small values of } r.$$

$$\frac{Zr}{a_0} > 2, \quad \psi_{2s} \text{ is negative;} \quad \text{true for large values of } r.$$

$$\text{and } \frac{Zr}{a_0} = 2, \quad \psi_{2s} \text{ is zero;} \quad \text{true at one particular value of } r.$$

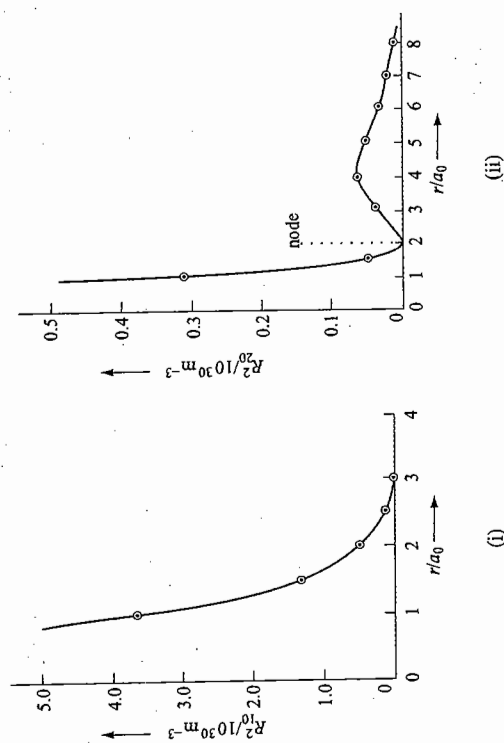
The point where the function has a zero value is known as the *nodal point*. In general, the number of *nodal points* in the radial function  $R_{n,l}$  is equal to  $(n - l - 1)$ .

Plots of  $R_{1s}^2$  and  $R_{2s}^2$ 

In chemistry, the plots of probability are more meaningful than the plots of the functions themselves. The probability is given as  $\psi^* \psi$  where  $\psi^*$  is the complex conjugate of  $\psi$  which is obtained by replacing  $i$  by  $-i$ . If the function does not involve  $i$ , then  $\psi^* \psi$  is simply equal to  $\psi^2$ . Figure 1.8.2 shows the probability plots for  $1s$  and  $2s$  orbitals.

† For the data, see Try Yourself Problem 1.22.

Fig. 1.8.2 Probability distribution for the electron in (i)  $1s$  and (ii)  $2s$  orbitals of the hydrogen atom



It can be seen from Fig. 1.8.2 that for both  $1s$  and  $2s$  orbitals, the probability has a maximum value at  $r = 0$ , i.e. on the nucleus. For  $2s$  orbital, one more maximum in the probability plot is observed.

## Dot-Population Diagrams

Three dimensional plots of  $\psi^* \psi$  versus  $r$  are shown by either dot-population picture (or the cloud density pattern), or by the equal-probability contour (or the boundary surface) plots. In the dot-population picture, we exhibit the relative probability at a given location by the density of dots near that location. For  $1s$  and  $2s$  orbitals, these dot-population pictures are shown in Fig. 1.8.3.



Fig. 1.8.3 The dot-population pictures (or the cloud density patterns) for  $1s$  and  $2s$  orbitals

The dot-population pictures give the most realistic description of the electron's time average distribution.

### Equal-Probability Contour Diagrams

In the equal-probability contours, we draw the contours by joining the points of identical probability. For s-orbitals, these contours are spherical in nature. If we are contended with a total of about 90% probability (a fairly large probability) of finding the electron, we can draw a contour within which there exists a total of about 90% probability of finding the electron. This gives us a definite shape in three dimensions and is known as the shape of the orbital. Note that if we want to account for 100% probability, we have to cover a very large distance from the nucleus, theoretically up to infinity. For 1s and 2s orbitals, the 90% probability contours are shown in Fig. 1.8.4.

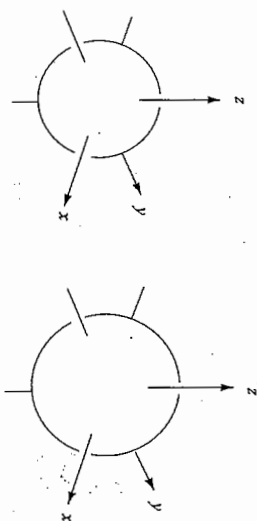


Fig. 1.8.4 90% probability contours for 1s and 2s orbitals

### Plots of Radial Distribution Functions

Though the probability of finding the electron in s-orbitals is maximum near to the nucleus, the total amount of the dot population (or the electronic cloud) near the nucleus is very small owing to the small volume near the nucleus. In order to visualize the total amount of the cloud within a spherical shell placed at radii  $r$  and  $r + dr$  from the nucleus, we define the radial distribution function,  $F_R$ , as

$$F_R = (\text{volume of the spherical shell}) (\text{probability density}) \\ = (4\pi r^2 dr) (R^2) \quad (1.8.2)^{\dagger}$$

Thus, the radial distribution function describes the total probability of finding the electron in a spherical shell of thickness  $dr$  located at the distance  $r$  from the nucleus.

**Note:** Strictly speaking, the charge within the shells of radii  $r$  and  $r + dr$  is given by

$$\rho = \int_r^{r+dr} R^2 r^2 dr \int_0^\pi \Theta^2 \sin \theta d\theta \int_0^{2\pi} \Phi^2 d\phi$$

For the normalized  $\Theta$  and  $\Phi$  functions, integrations over  $\theta$  and  $\phi$  yield unity. Hence, the above expression is reduced to

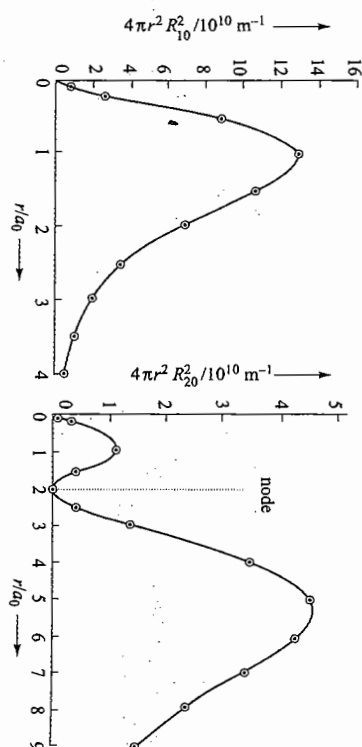
$$\rho = \int_r^{r+dr} r^2 R^2 dr$$

Thus, a plot of  $r^2 R^2$  versus  $r$  provides this information.

<sup>†</sup> Volume of the spherical shell of thickness  $dr$  and at the distance  $r$  from the nucleus,  $dV = (4/3)\pi(r + dr)^3 - (4/3)\pi r^3 = (4/3)\pi (dr^3 + 3r^2 dr + 3rdr^2)$ . Neglecting the terms involving  $dr^3$  and  $dr^2$ , we get  $dV = 4\pi r^2 dr$ .

For 1s and 2s orbitals, the radial distribution function versus  $r/a_0$  plots are shown in Fig. 1.8.5.

Fig. 1.8.5 Radial distribution function for the electron in 1s and 2s orbitals



The value of  $r$  at which the maximum in the radial distribution function plot for 1s orbital is observed is equal to  $a_0$ , i.e. 52.9 pm—a value which is exactly the same as that calculated from the Bohr's theory. Thus, we see that the Bohr's concept of orbit is partially explained by the quantum mechanical treatment, but the very existence of the precise orbit in an atom has no place in the quantum mechanical treatment. What quantum mechanics says that the electron has some probability for its existence at all values of  $r$ , but it has a maximum value per unit radius ( $dr = 1$ ) at a distance  $r = a_0$ .

For the 2s orbital, there are two maxima in the radial distribution plot, one at about 0.04 nm and the other at about 0.3 nm. The maximum at 0.04 nm is smaller than that at 0.3 nm. In general, the number of maxima in the radial distribution plot of s orbitals is equal to the principal quantum number. Out of these maxima, the last maximum which is situated at the largest value of  $r$  has the maximum height and the others have smaller heights.

### Problem 1.8.1

#### Solution

Show that in a hydrogen-like ion, the radius at which there is maximum probability of finding a 1s electron in any direction is  $a_0/Z$ , where  $Z$  is the nuclear charge and  $a_0$  is the Bohr radius of the first hydrogen orbit.

In order to find the value of  $r$  at which maximum probability is observed, we differentiate the radial distribution function with respect to  $r$  and equate the resultant expression to zero. Taking the radial distribution function simply as  $r^2 R_{1,0}^2$  without constant terms, we get

$$\frac{d}{dr} (r^2 R_{1,0}^2) = \frac{d}{dr} (r^2 e^{-2Zr/a_0}) \\ = 2r e^{-2Zr/a_0} + r^2 \left( -\frac{2Z}{a_0} \right) e^{-2Zr/a_0}$$

$$= 2r \left( 1 - \frac{Zr}{a_0} \right) e^{-2Zr/a_0}$$

$$\text{Thus } 2r \left( 1 - \frac{Zr}{a_0} \right) e^{-2Zr/a_0} = 0$$

and hence either  $r = 0$  or  $r = a_0/Z$  or  $r = \infty$  (from  $R_{1,0}^2$ ).

At  $r = 0$  and  $r = \infty$ , we observe two minima and hence the maximum is observed at  $a_0/Z$ .

### Plot of Functions of 2p-type

The various functions of  $p$ -type ( $l = 1$ ) with the same value of  $n$  but with different values of  $m$  will have the same  $r$ -dependent function since the latter depends only on the values of  $n$  and  $l$  and not on the value of  $m$ . For  $n = 2$ , the  $r$ -dependent function is

$$R_{2,1} = \frac{1}{\sqrt{3}} \left( \frac{Z}{2a_0} \right)^{3/2} \left( \frac{Zr}{a_0} \right) \exp(-Zr/2a_0) \quad (1.8.3)$$

It is obvious that

- The 2p-wave functions will not show any node at finite values of  $r$ . This is consistent with the general formula  $(n - l - 1)$  for the number of nodes in a wave function.
- The 2p-wave functions have zero value at  $r = 0$ .

Figure 1.8.6 depicts the plots of functions  $R_{2,1}$ ,  $R_{2,1}^2$  and  $4\pi r^2 R_{2,1}^2$  versus  $r$ .†

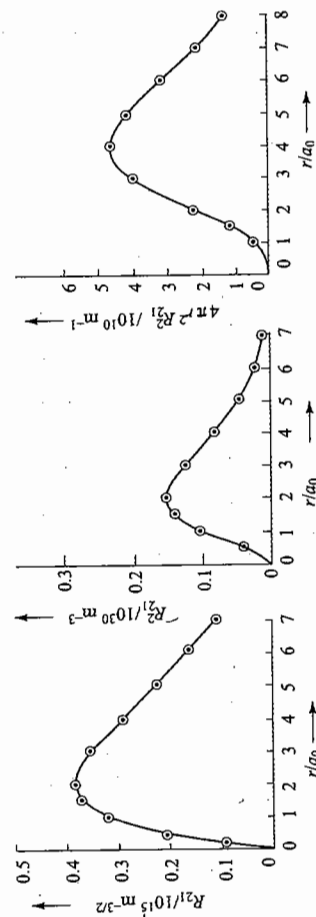


Fig. 1.8.6 Plots of  $R_{2,1}$ ,  $R_{2,1}^2$  and  $4\pi r^2 R_{2,1}^2$  versus  $r/a_0$  for the hydrogen atom

The  $r$ -dependence shown in Fig. 1.8.6 is spherically symmetric. However, this symmetry is lost due to the presence of angular functions which depends on the value of  $m$ .

† For the data, see Try Yourself Problem 1.22.

### Shape of 2p<sub>z</sub> orbital

For  $m = 0$ , the angular wave functions are

$$\Theta_{1,0} = \frac{\sqrt{6}}{2} \cos \theta \quad \text{and} \quad \Phi_0 = \frac{1}{\sqrt{2\pi}} \quad (1.8.4)$$

Since the function  $\Phi_0$  does not contain any  $\varphi$  dependence term, the function  $\psi_{2,1,0}$  (written as  $2p_z$ ) exhibits only  $\theta$ -dependence.

Two-dimensional plot of the function  $\Theta_{1,0}\Phi_0$  versus  $\theta$  would look like two circles in the  $xz$ -plane (or  $yz$ -plane); one just above the  $xy$ -nodal plane and the other just below it.† These two circles pass through the origin and are symmetrically placed about the  $z$ -axis (Fig. 1.8.7a). The values of the function  $\Theta\Phi$  for the various values of  $\theta$  are given by the lengths of the radial coordinate. This radial coordinate will have maximum positive and negative values along the  $z$ -axis when  $\theta = 0$  and  $\theta = \pi$ , respectively. On the  $xy$ -plane, the angle  $\theta = \pi/2$  and thus  $\cos \theta = 0$ . Hence the two circles pass through the origin, which serves as nodal point for the function  $\Theta\Phi$ . Since the angular part of the function  $\psi_{2,1,0}$  has its maximum along the  $z$ -axis, this orbital is referred to as the  $p_z$  orbital.

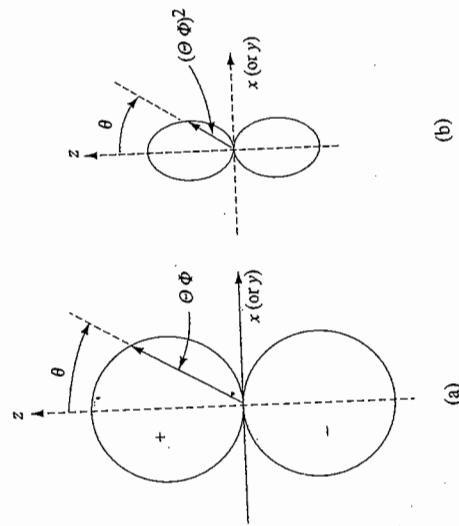


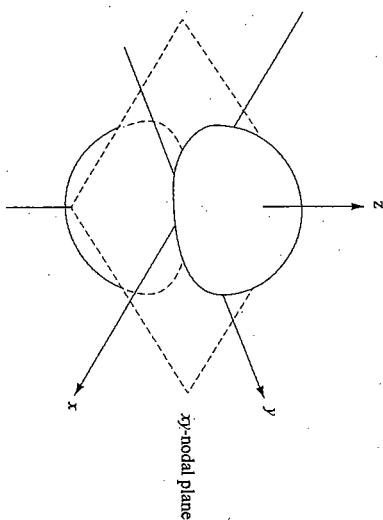
Fig. 1.8.7 (a) A two-dimensional plot of  $\Theta_{1,0}\Phi_0$  in the  $xz$ -plane or  $yz$ -plane against the angle  $\theta$ ; and (b) A two-dimensional plot of  $(\Theta_{1,0}\Phi_0)^2$  in the  $xz$ -plane or  $yz$ -plane against the angle  $\theta$

Alternatively, the angular dependence can be shown by a graph where  $(\Theta\Phi)^2$  is plotted against  $\theta$ . This plot is also shown in Fig. 1.8.7b.

The three-dimensional plot of  $2p_z$  orbital is obtained by rotating the curves of Fig. 1.8.7 about the  $z$ -axis.

A complete description of the function  $\psi_{2,1,0}$  (or  $\psi_{2,1,0}^2$ ) can be obtained by combining the radial and angular dependences. We can draw 90% probability contour diagram to give us the shape of  $2p_z$  orbital. This looks like two spheroidal lobes, with the nucleus located between them in the nodal plane as shown in Fig. 1.8.8.

† The number of nodal surfaces in the angular distribution function is equal to the value of quantum number  $l$ .

Fig. 1.8.8 90% probability contour diagram of the orbital  $2p_z$ .**Shapes of  $2p_x$  and  $2p_y$  orbitals**

Coming to the function  $\psi_{2,1,1}$  and  $\psi_{2,1,-1}$  we find that

$$\Theta_{1,\pm 1} = \frac{\sqrt{3}}{2} \sin \theta \quad (1.8.5)$$

$$\Phi_{+1} = \frac{1}{\sqrt{2\pi}} \exp(i\varphi) \quad (1.8.6)$$

$$\text{and} \quad \Phi_{-1} = \frac{1}{\sqrt{2\pi}} \exp(-i\varphi) \quad (1.8.7)$$

The functions  $\psi_{2,1,1}$  and  $\psi_{2,1,-1}$  also exhibit  $\varphi$  dependence. Since the functions  $\Phi$  involve the imaginary quantity  $i$ , these cannot be plotted directly.

However, this difficulty can be overcome by constructing a new but equivalent set of real wave functions through linear combination of the two wave functions  $\Phi_{+1}$  and  $\Phi_{-1}$ . Since the orbitals  $\Phi_{+1}$  and  $\Phi_{-1}$  are degenerate, any linear combination of these two wave functions will also be an eigenfunction of the  $\varphi$  dependent equation. We construct the following two linear combinations.

$$\Phi_x = \frac{1}{\sqrt{2}} (\Phi_{+1} + \Phi_{-1}) \quad (1.8.8)$$

$$\text{and} \quad \Phi_y = \frac{-i}{\sqrt{2}} (\Phi_{+1} - \Phi_{-1}) \quad (1.8.9)$$

Substituting the expressions of  $\Phi_{+1}$  and  $\Phi_{-1}$ , we get

$$\Phi_x = \frac{1}{\sqrt{2}} \left( \frac{1}{\sqrt{2\pi}} e^{i\varphi} + \frac{1}{\sqrt{2\pi}} e^{-i\varphi} \right) \quad (1.8.10)$$

$$\text{and} \quad \Phi_y = \frac{-i}{\sqrt{2}} \left( \frac{1}{\sqrt{2\pi}} e^{i\varphi} - \frac{1}{\sqrt{2\pi}} e^{-i\varphi} \right) \quad (1.8.11)$$

Now, according to Euler's formula, we have

$$e^{i\varphi} = \cos \varphi + i \sin \varphi$$

$$\text{and} \quad e^{-i\varphi} = \cos \varphi - i \sin \varphi$$

$$\text{and thus} \quad e^{i\varphi} + e^{-i\varphi} = 2 \cos \varphi$$

$$\text{and} \quad e^{i\varphi} - e^{-i\varphi} = 2i \sin \varphi$$

With these, the functions  $\Phi_x$  and  $\Phi_y$  become

$$\Phi_x = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2\pi}} 2 \cos \varphi = \frac{1}{\sqrt{\pi}} \cos \varphi \quad (1.8.12)$$

$$\text{and} \quad \Phi_y = \frac{-i}{\sqrt{2}} \frac{1}{\sqrt{2\pi}} (2i \sin \varphi) = \frac{1}{\sqrt{\pi}} \sin \varphi \quad (1.8.13)$$

Along the  $x$ -axis on the  $xy$ -plane, the angle  $\varphi$  is either zero or  $\pi$ , and thus  $\cos \varphi = 1$ . Hence the function  $\Phi_x$  will have maximum magnitude along the  $x$ -axis. It is because of this reason, the subscript  $x$  has been added to the function  $\Phi$ . Similarly, the function  $\Phi_y$  will have maximum magnitude along the  $y$ -axis where the angle  $\varphi$  takes the value of either  $\pi/2$  or  $3\pi/2$ . Now, if the functions  $\Phi_x$  and  $\Phi_y$  are combined with the  $\Theta$  function, we get the complete angular dependence of the orbitals  $2p_x$  and  $2p_y$ , respectively.

$$2p_x \text{ orbital:} \quad \Theta \Phi_x = \left( \frac{\sqrt{3}}{2} \sin \theta \right) \left( \frac{1}{\sqrt{\pi}} \cos \varphi \right) \quad (1.8.14)$$

$$2p_y \text{ orbital:} \quad \Theta \Phi_y = \left( \frac{\sqrt{3}}{2} \sin \theta \right) \left( \frac{1}{\sqrt{\pi}} \sin \varphi \right) \quad (1.8.15)$$

If the function ( $\Theta \Phi$ ) is plotted for different values of  $\theta$  at constant  $\varphi$  angles equal to 0 and  $\pi$  (or keeping  $\theta$  constant at  $\pi/2$  and varying angle  $\varphi$  from 0 to  $2\pi$ ), we get the two-dimensional angular plot of  $2p_x$  orbital in  $xz$ -plane (or  $xy$ -plane). The general shape of the plot is identical to that of  $2p_z$  orbital (Fig. 1.8.7a). Similarly, the function ( $\Theta \Phi_y$ ) may be plotted for different values of  $\theta$  at constant  $\varphi$  angles equal to  $\pi/2$  and  $3\pi/2$  (or keeping  $\theta$  constant at  $\pi/2$  and varying angle  $\varphi$  from 0 to  $2\pi$ ) to give the corresponding two-dimensional angular plot of  $2p_y$  orbital in the  $yz$ -plane (or  $xy$ -plane). The shape of the plot is the same as those of  $2p_z$  and  $2p_x$  plots. The two circles of  $2p_x$  orbital lie symmetrically about the  $x$ -axis (with  $yz$ -nodal plane) whereas those of  $2p_y$  orbital lie symmetrically about the  $y$ -axis (with  $xz$ -nodal plane).

The complete description of the function  $\psi_{2p_x}$  (or  $\psi_{2p_y}^2$ ) and  $\psi_{2p_y}$  (or  $\psi_{2p_x}^2$ ) can be obtained by combining the above angular dependence with the radial distribution shown in Fig. 1.8.6. As usual, 90% probability contour diagrams can be drawn to provide the shapes of  $2p_x$  and  $2p_y$  orbitals. Obviously, they will have the same appearance as that of  $2p_z$  orbital, the two spheroidal lobes of these orbitals point along  $x$ - and  $y$ -axis, respectively (Fig. 1.8.9).



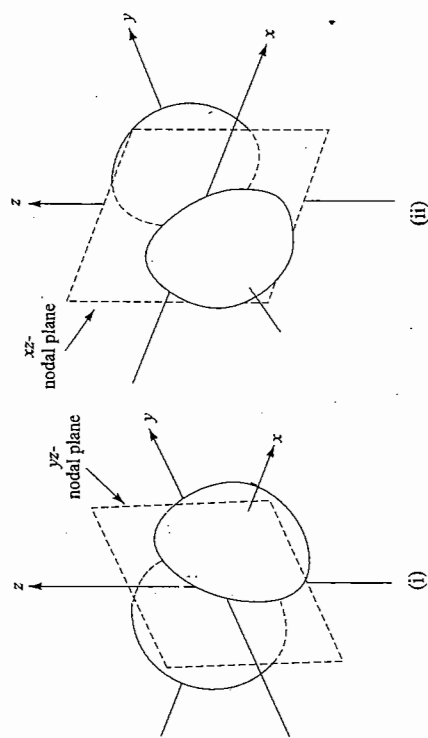


Fig. 1.8.9 90% probability contour of (i)  $2p_x$  and (ii)  $2p_y$  orbitals

### Plots of 3p Wave Functions

Coming to 3p orbitals, we observe that the radial function is given as

$$R_{3,1} = \frac{2\sqrt{2}}{9} \left( \frac{Z}{3a_0} \right)^{3/2} \left( \frac{2Zr}{a_0} - \frac{Z^2 r^2}{3a_0^2} \right) \exp(-Zr/3a_0) \quad (1.8.16)$$

Obviously, this function will show one node at a distance of  $r = 6a_0/Z$ . The directional characteristics of 3p orbitals will be exactly identical to those of 2p orbitals. Thus, we will have  $3p_x$ ,  $3p_y$  and  $3p_z$  orbitals pointing along the x, y, and z-axes, respectively. The 90% probability contour of  $3p_z$  orbital is shown in Fig. 1.8.10.

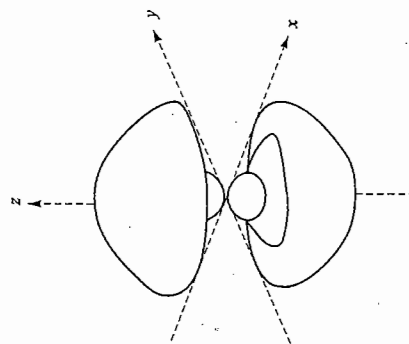


Fig. 1.8.10 90% probability contour of  $3p_z$  orbital

### Plots of Functions of 3d Orbitals

At the very outset, it may be stated that the 3d orbitals do not contain any radial node as  $n - l - 1 = 3 - 2 - 1 = 0$ . Only the directional characteristics of these orbitals are discussed here. The angular functions of these orbitals are as follows.

$$\theta_{2,0} = \frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1); \quad \Phi_0 = \frac{1}{\sqrt{2\pi}} \quad (1.8.17)$$

### Plot of $\theta_{2,0}$ , $\Phi_0$

The plot of  $(\theta_{2,0}, \Phi_0)$  can be carried out directly as it does not involve any imaginary quantity. The value of the function  $\theta_{2,0}$  is zero when  $3 \cos^2 \theta - 1 = 0$  or  $\cos \theta = \pm 1/\sqrt{3}$  or  $\theta = \pm 54^\circ 44'$ . Thus, a line passing through the origin making an angle  $\theta = 54^\circ 44'$  with the z-axis will be the nodal line. Since this type of line can be drawn all around the z-axis, we have nodal surfaces making cones about the z-axis, as shown in Fig. 1.8.11. The 90% probability contour of  $3d_0$  orbital (or  $3d_{z^2}$ ) is also shown in Fig. 1.8.11. The angular dependence  $3 \cos^2 \theta - 1$  corresponds to  $2z^2 - x^2 - y^2$  which is approximately written as  $z^2$ .

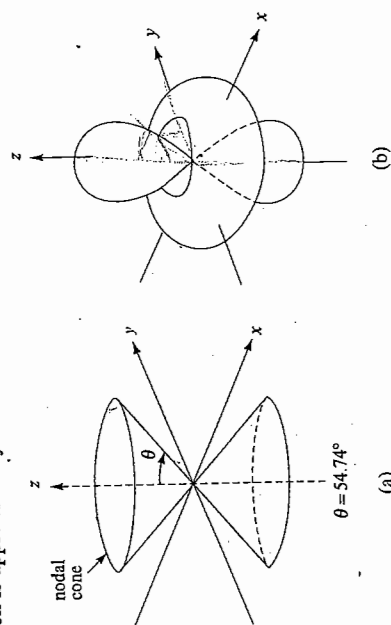


Fig. 1.8.11 (a) Nodal surfaces forming two cones about z-axis of  $3d_{z^2}$  orbital (b) 90% probability contour diagram of  $3d_{z^2}$  orbital

### Linear Combinations of the Remaining $\Phi$ Functions

The functions  $\Phi_{+1}$ ,  $\Phi_{-1}$ ,  $\Phi_{+2}$  and  $\Phi_{-2}$  involve imaginary quantity  $i$ , and thus these cannot be plotted as such. However, real functions can be constructed by taking linear combinations of them as follows:

$$\Phi_x = \frac{\Phi_{+1} + \Phi_{-1}}{\sqrt{2}} = \frac{1}{\sqrt{\pi}} \cos \varphi \quad (1.8.20)$$

$$\Phi_y = -i \left( \frac{\Phi_{+1} - \Phi_{-1}}{\sqrt{2}} \right) = \frac{1}{\sqrt{\pi}} \sin \varphi \quad (1.8.21)$$

$$\Phi_{x^2 - y^2} = \frac{\Phi_{+2} + \Phi_{-2}}{\sqrt{2}} = \frac{1}{\sqrt{\pi}} \cos 2\varphi \quad (1.8.22)$$

$$\text{and } \Phi_{xy} = -i \left( \frac{\Phi_{+2} - \Phi_{-2}}{\sqrt{2}} \right) = \frac{1}{\sqrt{\pi}} \sin 2\varphi \quad (1.8.23)$$

### Expressions of Total Angular Functions

Thus, the total angular functions for the rest of the four 3d orbitals are given by

$$(\Theta_{2,\pm 1}\Phi_y) = \left(\frac{15}{4\pi}\right)^{1/2} \sin \theta \cos \theta \cos \phi \quad (1.8.24)$$

$$(\Theta_{2,\pm 1}\Phi_z) = \left(\frac{15}{4\pi}\right)^{1/2} \sin \theta \cos \theta \sin \phi \quad (1.8.25)$$

$$(\Theta_{2,\pm 2}\Phi_{xy}) = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \theta \sin 2\phi \quad (1.8.26)$$

$$\text{and } (\Theta_{2,\pm 2}\Phi_{x^2-y^2}) = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \theta \cos 2\phi \quad (1.8.27)$$

Each of the functions given above has two nodal surfaces. A brief description of these nodal surfaces is in order.

The value of this function will be zero when  $\theta = 0^\circ$  or  $90^\circ$  and  $\phi = 90^\circ$ . When  $\theta \neq 0$  and  $\phi = 90^\circ$ , we have yz-plane as the nodal surface and when  $\theta = 90^\circ$ , the nodal surface is xz-plane. These nodal surfaces are shown in Fig. 1.8.12a. This function can also be written as

$$(\Theta_{2,\pm 1}\Phi_z) = \left(\frac{15}{4\pi}\right)^{1/2} \frac{\sin 2\theta}{2} \cos \phi \quad (1.8.28)$$

Equation (1.8.28) will have a maximum value when  $\cos \phi = 1$  and  $\sin 2\theta = 1$ , i.e. when  $\phi = 0^\circ$  and  $2\theta = 90^\circ$  or  $\theta = 45^\circ$ . If we construct a two-dimensional plot of the function keeping all the while angle  $\phi$  equal to  $0^\circ$  and varying  $\theta$ , we get four lobes lying symmetrically between the axial directions, viz., between x- and z-axes as shown in Fig. 1.8.12b. These lobes, lie on the xz-plane and it is for this reason this orbital is referred to as  $d_{xz}$ . When the radial distribution is incorporated along with the variation of  $\phi$ , we get four lobes in three dimensions describing the 90% probability contour diagram (represented as  $3d_{xz}$  orbital). The subscript xz also corresponds to the angular dependence ( $\sin \theta \cos \phi$ )( $\cos \theta$ ).

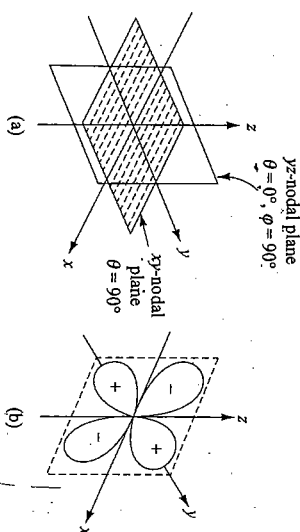


Fig. 1.8.12 (a) Two nodal surfaces yz and xy, (b) A two-dimensional plot of function  $(\Theta_{2,\pm 1}\Phi_z)$

### Nodal Surfaces in $\Theta_{2,\pm 1}\Phi_y$

The value of this function will be zero when  $\theta = 0^\circ$  or  $90^\circ$  and  $\phi = 0^\circ$ . When  $\theta = 0^\circ$  and  $\phi = 0^\circ$ , we have xz-plane as the nodal surface and when  $\theta = 90^\circ$ , the nodal surface is xy-plane (Fig. 1.8.13a). An alternative form of this function is

$$(\Theta_{2,\pm 1}\Phi_y) = \left(\frac{15}{4\pi}\right)^{1/2} \frac{\sin 2\theta}{2} \sin \phi \quad (1.8.29)$$

Equation (1.8.29) will have a maximum value when  $\sin \phi = 1$  and  $\sin 2\theta = 1$ , i.e. when  $\phi = 90^\circ$  and  $\theta = 45^\circ$ . If we construct a two-dimensional plot of the function keeping all the while  $\phi = 90^\circ$  and varying  $\theta$ , we get four lobes lying symmetrically between y- and z-axes as shown in Fig. 1.8.13b. These lobes lie on the yz-plane and it is for this reason this orbital is labelled as  $3d_{yz}$ . The subscript yz also corresponds to the angular dependence ( $\sin \theta \sin \phi$ )( $\cos \theta$ ).

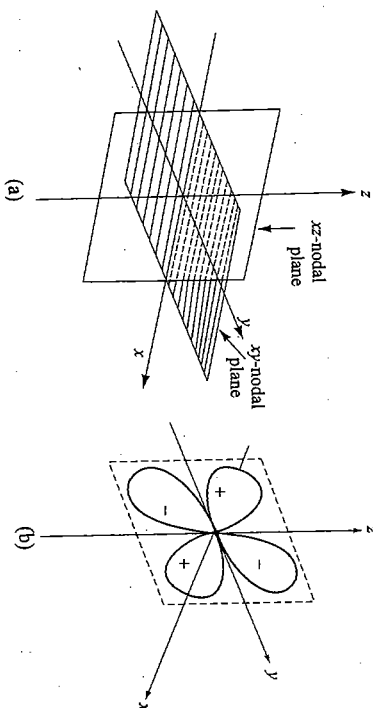


Fig. 1.8.13 (a) The two nodal surfaces xy and xz, (b) A two-dimensional plot of function  $(\Theta_{2,\pm 1}\Phi_y)$

### Nodal Surfaces in $\Theta_{2,\pm 2}\Phi_{xy}$

The value of this function will be zero when  $\theta = 0$ , and  $\phi = 0$  and  $90^\circ$ . When  $\theta = 0$  and  $\phi = 0$ , we have xz-plane as the nodal surface and when  $\theta = 0$  and  $\phi = 90^\circ$ , the nodal surface is yz-plane. These surfaces are shown in Fig. 1.8.14a. This function will have a maximum value when  $\sin \theta = 1$  and  $\sin 2\phi = 1$ , i.e. when  $\theta = 90^\circ$  and  $\phi = 45^\circ$ . If we construct a two-dimensional plot of the function keeping all the while  $\theta = 90^\circ$  and varying  $\phi$ , we get four lobes lying symmetrically between x- and y-axes (Fig. 1.8.14b). These lobes lie on the xy-plane and it is for this reason this orbital is labelled as  $3d_{xy}$ . The subscript xy also corresponds to the angular dependence ( $\sin \theta \cos \phi$ )( $\sin \theta \sin \phi$ ).

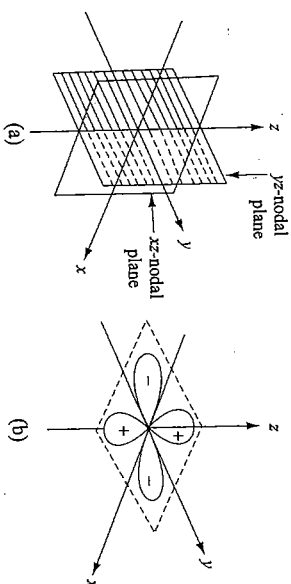


Fig. 1.8.14 (a) The two nodal surfaces xz and yz, (b) A two-dimensional plot of function  $(\Theta_{2,\pm 2}\Phi_{xy})$

### Nodal Surfaces in $\Theta_{2,\pm 2}\Phi_{x^2-y^2}$

The value of this function is zero when  $\theta = 0$ , and  $\phi = 45^\circ$ , and  $\phi = -45^\circ$ . Thus two nodal surfaces are generated when (i)  $\theta = 0$  and  $\phi = 45^\circ$ , and (ii)  $\theta = 0$  and  $\phi = -45^\circ$ . These surfaces just lie in between x- and y-axes and include z-axis in them, as shown in Fig. 1.8.15a.

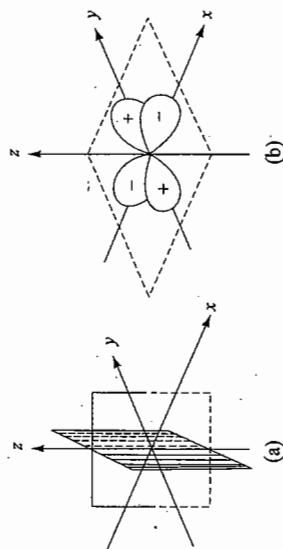


Fig. 1.8.15 (a) Two nodal surfaces at angle  $45^\circ$  to  $x$  and  $y$  axes, (b) A two-dimensional plot of the function  $(\Theta_{x, z} \Phi_{x^2 - y^2})$

This function will have a maximum value when  $\sin \theta = 1$  and  $\cos 2\phi = 1$ , i.e. when  $\theta = 90^\circ$  and  $\phi = 0$  or  $90^\circ$ . Thus, when a two-dimensional plot is constructed keeping all the while  $\theta = 90^\circ$  and varying  $\phi$ , we get four lobes lying on the  $x$ - and  $y$ -axes (Fig. 1.8.15b). It is for this reason, the present function is named as  $(3d_{x^2 - y^2})$ . The subscript  $x^2 - y^2$  corresponds to the angular dependence  $\sin^2 \theta \cos^2 \phi - \sin^2 \theta \sin^2 \phi$ .

## 1.9 ANGULAR MOMENTUM AND THE MAGNETIC MOMENT

### Classical Expression of Magnetic Moment

A current flowing in a coil of wire of ordinary dimensions produces a magnet. The orientation of the magnet is such that it produces a magnetic field perpendicular to the plane of the coil. The magnetic moment of the magnet can be calculated from the Ampere's law

$$\mu_m = iA \quad (1.9.1)$$

where  $i$  is the current circulating in the coil per unit time and  $A$  is the area of cross-section of the coil.

In classical mechanics, the orbital motion of an electron corresponds to the passage of current through a coil of wire. Consequently, a tiny magnet is associated with the orbital motion of the electron. The magnetic moment of this tiny magnet can be determined as follows.

Let  $v$  be the speed of the electron revolving in an orbit of radius  $r$ . The current  $i$  circulating in the orbit will be given as

$$i = (\text{number of revolutions/second}) (\text{electronic charge})$$

$$= - \left( \frac{v}{2\pi r} \right) e \quad (1.9.2)$$

The negative sign in Eq. (1.9.2) is due to the fact that the electron is negatively-charged particle. The area of cross-section  $A$  of the orbit is

$$A = \pi r^2 \quad (1.9.3)$$

Substituting Eqs (1.9.2) and (1.9.3) in Eq. (1.9.1), we get

$$\mu_m = \left( - \frac{ve}{2\pi r} \right) (\pi r^2) = - \frac{v r e}{2}$$

Multiplying and dividing by  $m_e$ , we get

$$\mu_m = - (m_e v r) \left( \frac{e}{2m_e} \right) = - L \left( \frac{e}{2m_e} \right) \quad (1.9.4)$$

where  $L$  is the angular momentum of the electron. Equation (1.9.4) is usually written as

$$\mu_m = - g L \quad (1.9.5)$$

where  $g$  is equal to  $e/2m_e$ . The factor  $g$  represents the ratio of magnetic moment to the angular momentum and is known as the *gyromagnetic ratio*. Both angular momentum and magnetic moment are vector quantities. These two quantities are directed along the axis normal to the plane of the current loop. The negative sign in Eq. (1.9.5) tells that the magnetic moment vector has a direction opposite to that of the angular momentum vector as shown in Fig. 1.9.1.

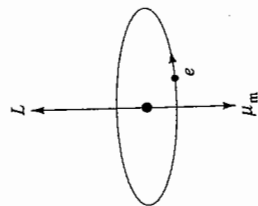


Fig. 1.9.1 The magnetic moment vector associated with the orbital motion of the electron

### Quantum Mechanical Expression of Magnetic Moment

The above classical treatment can be converted to the correct quantum mechanical treatment. According to quantum mechanics, the orbital angular momentum of the electron is quantized and is given by

$$L = \sqrt{l(l+1)} \left( \frac{h}{2\pi} \right)$$

where  $l$  is the azimuthal quantum number. Substituting the above relation in Eq. (1.9.4), we get

$$\mu_m = - \left( \frac{eh}{4\pi m_e} \right) \left( \sqrt{l(l+1)} \right) \quad (1.9.6)$$

Equation (1.9.6) is written as

$$\mu_m = - \mu_B \sqrt{l(l+1)} \quad (1.9.7)$$

where  $\mu_B$  is equal to  $eh/4\pi m_e$  and is known as *Bohr magneton*. Its value is

$$\begin{aligned} \mu_B &= \frac{eh}{4\pi m_e} = \frac{(1.6 \times 10^{-19} \text{ C})(6.626 \times 10^{-34} \text{ J s})}{4(3.14)(9.1 \times 10^{-31} \text{ kg})} \\ &= 9.274 \times 10^{-24} \text{ J T}^{-1} \end{aligned}$$

It was seen earlier that the orbital angular momentum is space quantized, i.e. the angular momentum vector does not point in any arbitrary direction in space but points only along certain directions which are determined by the following condition

of quantization of  $z$ -component of the angular momentum.

$$L_z = m \left( \frac{h}{2\pi} \right) \quad (1.9.8)$$

where  $m$  is the magnetic quantum number. The allowed values of  $m$  are 0,  $\pm 1$ ,  $\pm 2$ , ...,  $\pm l$ . If  $\theta$  is the angle between the angular momentum vector and the  $z$ -axis, it is obvious that

$$\left( \sqrt{l(l+1)} \frac{h}{2\pi} \cos \theta \right) = m \left( \frac{h}{2\pi} \right)$$

$$\text{or } \left( \sqrt{l(l+1)} \right) \cos \theta = m \quad (1.9.9)$$

Since the magnetic moment vector has a direction opposite to that of angular momentum vector, it follows that the former, like angular momentum, will also be directed along certain directions in space such that

$$\mu_m \cos \theta = \mu_z \quad (1.9.10)$$

The  $z$ -direction in an atom is completely arbitrary. This direction, however, can be fixed by placing the atom either in a magnetic field or in an electrical field. The direction of the field is taken to be the  $z$ -axis. Since  $m$  can never be equal to  $\sqrt{l(l+1)}$ , it follows that  $\mu_z$  can never be equal to  $\mu_m$ , i.e. the magnitude of the magnetic moment vector and its component can never have the same value. This implies that the magnetic moment vector can never be aligned along the magnetic axis and hence it will always be oriented with respect to the  $z$ -axis. For  $l = 1$  the three allowed orientations of angular momentum and the magnetic moment are shown in Fig. 1.9.2.

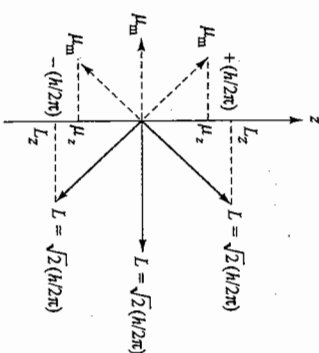


Fig. 1.9.2 The allowed orientations of angular momentum (solid arrows) and the magnetic moment (broken arrows) of an electron in  $l = 1$  state

### Larmor Precession

In the presence of a magnetic field, the magnetic moment vector executes *Larmor precession* around the magnetic field. This is basically due to the quantum mechanical restriction that the magnetic moment vector (or the angular momentum vector) can never be aligned along the magnetic field. What happens is that the magnetic moment experiences a couple force which tends to align the vector along the field direction. Classically, this alignment is permitted but quantum mechanically this is not possible. The only other effect of this force is to rotate the magnetic moment vector around the field direction, keeping all the while its orientation angle  $\theta$  constant. Thus, the magnetic moment vector starts precessing around the magnetic field.

### Potential Energy of an Electron in a Magnetic Field Due to its Orbital Motion

#### Energy of Electron in s Orbital

Since for  $s$  orbitals  $m = 0$ , it is obvious that the energy of  $s$  orbital remains unaffected in the presence of a magnetic field. This also follows from the fact that the angular momentum of electron in  $s$  orbital is zero and hence its magnetic moment is also zero, i.e. the motion of electron in  $s$  orbital is such that it does not produce any magnetic dipole and thus no interaction with the external magnetic field can take place.

#### Energy of Electron in p Orbital

The permitted values of  $m$  for  $p$  orbitals are  $+1$ ,  $0$  and  $-1$ . Hence the energy of electron in  $p$  orbitals gets modified to the following values.

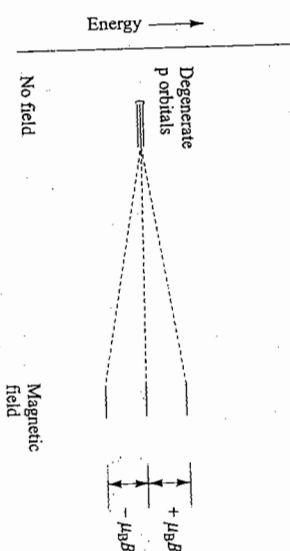
$$E_{n(l+1)} = E_n + B\mu_B \quad (1.9.13)$$

$$E_{n(0)} = E_n \quad (1.9.14)$$

$$E_{n(l-1)} = E_n - B\mu_B \quad (1.9.15)$$

Hence the degeneracy of the three  $p$  orbitals are removed in the presence of a magnetic field (Fig. 1.9.3).

Fig. 1.9.3 Lifting of degeneracy of  $p$  orbitals in the presence of a magnetic field



In general, the presence of a magnetic field removes the degeneracy with respect to the quantum number  $m$ . Thus,  $d$  orbitals which are fivefold degenerate become

nondegenerate with potential energies of  $2B\mu_B$ ,  $B\mu_B$ , 0,  $-B\mu_B$  and  $-2B\mu_B$ , respectively. Similarly,  $f$  orbitals split into seven orbitals all with different energies.

## 1.10 ZEEMAN AND ANOMALOUS ZEEMAN EFFECTS

### Zeeman Effect

Zeeman in 1886 observed that many of the spectral lines of an atom split into more than one line when placed in a magnetic field. This effect, known as the Zeeman effect, has been explained on the basis of the removal of degeneracy of orbitals having magnetic quantum number  $m$  greater than zero in the presence of a magnetic field. For example, the transition from any one of the three  $2p$  orbitals to  $1s$  orbital produces the same spectral line in the absence of a magnetic field, since all three  $2p$  orbitals are degenerate in energy. In the presence of a magnetic field, this degeneracy is no more present and according to the selection rules, the three transitions  $1s \leftarrow 2p_{+1}$ ,  $1s \leftarrow 2p_0$  and  $1s \leftarrow 2p_{-1}$  are possible. These are shown in Fig. 1.10.1.

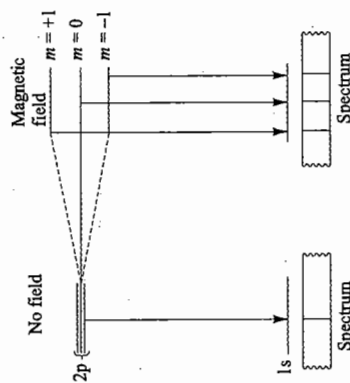


Fig. 1.10.1 Splitting of a single  $1s \leftarrow 2p$  spectral line into three lines in the presence of a magnetic field

### Anomalous Zeeman Effect

When the Zeeman effect is examined under high resolution microscope, the spectrum is found to be more complicated. In fact, a spectral line which appears to be a single one, actually consists of many lines closely placed to each other. For example, all the three transitions  $1s \leftarrow 2p_{+1}$ ,  $1s \leftarrow 2p_0$  and  $1s \leftarrow 2p_{-1}$  shown in Fig. 1.10.1 are actually made up of two closely packed lines. The existence of double lines instead of a single line is also observed in the spectra for the alkali metals even in the absence of a magnetic field.

### Quantum Numbers Describing Spinning of Electron

In order to explain the existence of doublets in the spectra of alkali metals, Goudsmit and Uhlenbeck in 1925 proposed that the electron has an intrinsic angular momentum due to spinning about its own axis. The value of the spin angular momentum is quite independent of the orbital angular momentum and can be described by two spin quantum numbers  $s$  and  $m_s$ . The physical significance of these numbers is very similar to those of orbital quantum numbers  $l$  and  $m$ . The quantum number  $s$  represents the total magnitude of the spin angular momentum  $S$  and the quantum number  $m_s$  represents the  $z$ -component of the angular momentum  $S_z$  such that

$$S = \sqrt{s(s+1)} \frac{h}{2\pi} \quad (1.10.1)$$

$$S_z = m_s \frac{h}{2\pi} \quad (1.10.2)$$

The relation between  $S$  and  $S_z$  is

$$S_z = S \cos \theta \quad (1.10.3)$$

where  $\theta$  is the angle which the angular momentum vector makes with  $z$ -axis. Substituting Eqs (1.10.1) and (1.10.2) in Eq. (1.10.3), we get

$$m_s = \sqrt{s(s+1)} \cos \theta \quad (1.10.4)$$

The allowed values of  $m_s$  are

$$-s, -(s-1), \dots, (s-1), s \quad (1.10.5)$$

It is found that the spin quantum number  $s$  has only one value of  $1/2$ . Thus, the magnitude of the spin angular momentum vector is

$$S = \sqrt{s(s+1)} \left( \frac{h}{2\pi} \right) = \sqrt{\frac{1}{2} \left( \frac{1}{2} + 1 \right)} \left( \frac{h}{2\pi} \right) = 0.866 \left( \frac{h}{2\pi} \right)$$

With  $s = (1/2)$ , the permitted values of  $m_s$  are  $+1/2$  and  $-1/2$ . Thus, the  $z$ -components of the spin angular momentum are given by

$$S_z = \pm \frac{1}{2} \left( \frac{h}{2\pi} \right)$$

Only two orientations of the spin angular momentum are possible. These are shown in Fig. 1.10.2. Since the spin angular momentum has only a single value, it is not describable by classical mechanics. It is strictly a nonclassical concept.

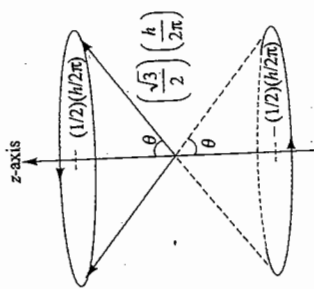


Fig. 1.10.2 Space quantization of spin angular momentum

### Magnetic Moment Due to Spin of Electron

The spinning of the electron will be associated with the magnetic moment vector which will have its direction opposite to that of the angular momentum vector. The relation connecting the magnetic moment  $\mu$  and the angular momentum  $S$  is

$$\mu = -gS \quad (1.10.6)$$

where  $g$  is equal to  $e/2m_e$ . The factor 2 in Eq. (1.10.6) has been added on the basis of experimental evidence (e.g. the examination of the splitting of the spectral lines in magnetic field). This implies that the gyromagnetic ratio for the spinning of electron is twice as large as that of the orbital motion of the electron.

Substituting the value of  $S$  from Eq. (1.10.1) in Eq. (1.10.6), we have

$$\mu = -2 \left( \frac{gh}{2\pi} \right) \sqrt{s(s+1)}$$

Substituting the expression of  $g$ , we have

$$\mu = -2 \left( \frac{eh}{4\pi m_e} \right) \sqrt{s(s+1)} = -2\mu_B \sqrt{s(s+1)} \quad (1.10.7)$$

where  $\mu_B$  is the Bohr magneton.

The potential energy of the spinning electron in the presence of a magnetic field is given by

$$V = -B\mu_z = -B(\mu \cos \theta)$$

Substituting  $\mu$  from Eq. (1.10.7), we have

$$V = -B \left\{ -2\mu_B \sqrt{s(s+1)} \right\} \cos \theta$$

which on making use of Eq. (1.10.4) becomes

$$V = 2B\mu_B m_s \quad (1.10.8)$$

According to Eq. (1.10.8), the potential energy of an electron depends on the value of  $m_s$ . Thus, we will have

$$(i) \quad m_s = +1/2; \quad V_{+1/2} = B\mu_B \quad (1.10.9)$$

$$(ii) \quad m_s = -1/2; \quad V_{-1/2} = -B\mu_B \quad (1.10.10)$$

In the presence of a magnetic field, the orbital energy of an electron is given by  $E_n'' = E_n + B\mu_B m_l + 2B\mu_B m_s$  (1.10.11)

where  $E_n$  is energy of the electron in the absence of a magnetic field,  $B\mu_B m_l$  is the potential energy due to the orbital motion, and  $2B\mu_B m_s$  is the potential energy due to the spinning of the electron. Thus, we have

**For  $s$  orbital** Here  $m = 0$ . Therefore

$$E_n'' = E_n + 2B\mu_B m_s$$

and since  $m_s$  can have two values,  $+1/2$  and  $-1/2$ , the modified values of energy are:

$$m_s = +1/2; \quad E_{n, +1/2}'' = E_n + B\mu_B$$

$$m_s = -1/2; \quad E_{n, -1/2}'' = E_n - B\mu_B$$

**For  $p$  orbitals** Here, we can have the following combinations.

$$(i) \quad m_l = +1 \quad m_s = +1/2 \quad E_{n, +1, +1/2}'' = E_n + B\mu_B + B\mu_B = E_n + 2B\mu_B$$

$$(ii) \quad m_l = +1 \quad m_s = -1/2 \quad E_{n, +1, -1/2}'' = E_n + B\mu_B - B\mu_B = E_n$$

$$(iii) \quad m_l = 0 \quad m_s = +1/2 \quad E_{n, 0, +1/2}'' = E_n + B\mu_B$$

$$(iv) \quad m_l = 0 \quad m_s = -1/2 \quad E_{n, 0, -1/2}'' = E_n - B\mu_B$$

$$(v) \quad m_l = -1 \quad m_s = +1/2 \quad E_{n, -1, +1/2}'' = E_n - B\mu_B + B\mu_B = E_n$$

$$(vi) \quad m_l = -1 \quad m_s = -1/2 \quad E_{n, -1, -1/2}'' = E_n - B\mu_B - B\mu_B = E_n - 2B\mu_B$$

Figure 1.10.3 illustrates the modified values of energy of electron in  $1s$  and  $2p$  orbitals, which also exhibits the allowed spectral transitions.

The selection rules for the allowed transitions shown in Fig. 1.10.3 are the same as those listed in Section 1.7 with one additional rule of  $\Delta m_s = 0$ . The allowed transitions are listed in Table 1.10.1.

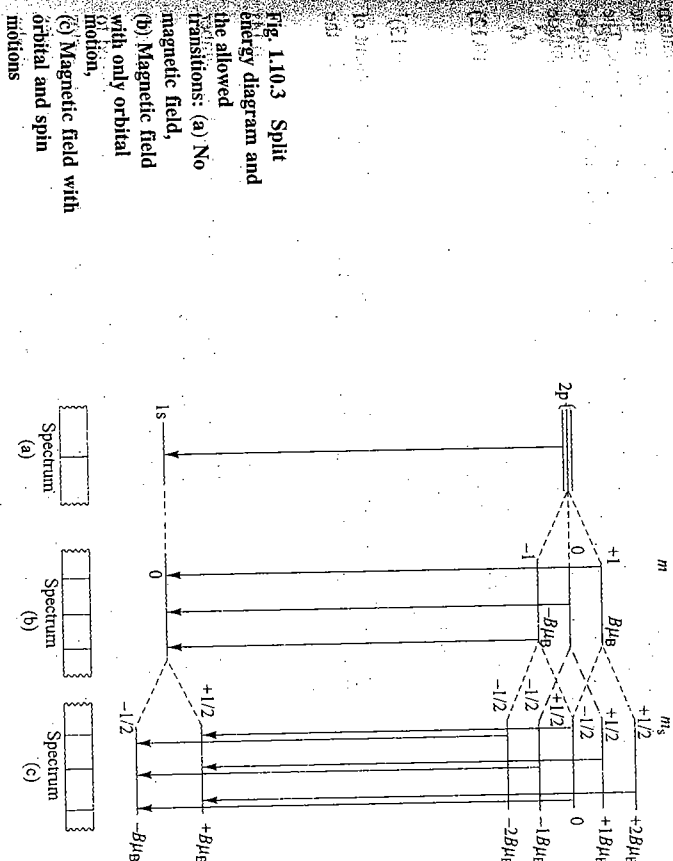


Table 1.10.1 The Allowed Electronic Transitions in the Presence of a Magnetic Field

Transition	Upper level	Lower level	Energy
$m = +1, m_s = +1/2 \longrightarrow m = 0, m_s = +1/2$	$E_{n, +1, +1/2}''$	$E_{n, 0, +1/2}''$	$\Delta E = (E_{n, +1, +1/2}'' - E_{n, 0, +1/2}'')$
$m = 0, m_s = +1/2 \longrightarrow m = 0, m_s = -1/2$	$E_{n, 0, +1/2}''$	$E_{n, 0, -1/2}''$	$\Delta E = (E_{n, 0, +1/2}'' - E_{n, 0, -1/2}'')$
$m = -1, m_s = +1/2 \longrightarrow m = 0, m_s = +1/2$	$E_{n, -1, +1/2}''$	$E_{n, 0, +1/2}''$	$\Delta E = (E_{n, -1, +1/2}'' - E_{n, 0, +1/2}'')$
$m = +1, m_s = -1/2 \longrightarrow m = 0, m_s = -1/2$	$E_{n, +1, -1/2}''$	$E_{n, 0, -1/2}''$	$\Delta E = (E_{n, +1, -1/2}'' - E_{n, 0, -1/2}'')$
$m = 0, m_s = -1/2 \longrightarrow m = 0, m_s = +1/2$	$E_{n, 0, -1/2}''$	$E_{n, 0, +1/2}''$	$\Delta E = (E_{n, 0, -1/2}'' - E_{n, 0, +1/2}'')$
$m = -1, m_s = -1/2 \longrightarrow m = 0, m_s = -1/2$	$E_{n, -1, -1/2}''$	$E_{n, 0, -1/2}''$	$\Delta E = (E_{n, -1, -1/2}'' - E_{n, 0, -1/2}'')$

### Spin-Orbit Coupling

From Fig. 1.10.3 and Table 1.10.1, it is obvious that the single line observed in the absence of magnetic field splits into three lines even if the electron spin is taken into account. The additional splitting of the lines cannot be explained unless we consider the relativistic treatment of the hydrogen atom, given by Dirac in 1928. One of the correction terms involves the interaction of orbital angular momentum and orbital magnetic moment vectors with the corresponding spin angular momentum and spin magnetic moment vectors. This is known as spin-orbit coupling. In the latter, the two vectors couple with each other and produce a resultant vector. The latter, like spin and orbital angular momentum vector, is also quantized and can be characterized by the total angular momentum quantum number,  $J$ . The magnitude of the resultant vector is given by the relation

$$L = \left\{ \sqrt{J(J+1)} \right\} \left\{ \frac{h}{2\pi} \right\} \quad (1.10.12)$$

The permitted values of  $J$  are

$$l + s, l + s - 1, \dots, l - s \quad (1.10.13)^\dagger$$

The total angular momentum is also space quantized, i.e. the  $z$ -component of the total angular momentum has only discrete values which are given by the relation

$$L_z = L \cos \theta = m_J \left\{ \frac{h}{2\pi} \right\} \quad (1.10.14)$$

where  $m_J$  is known as the magnetic total angular momentum quantum number and can have any one of the values given below:

$$J, J-1, \dots, -(J-1), -J \quad (1.10.15)$$

In a similar manner, the two magnetic moment vectors can be combined to give a resultant total magnetic moment vector. This total magnetic moment vector does not lie along the direction of total orbital momentum, since the magnitudes of the two magnetic moment vectors do not bear the same relation with the corresponding magnitude of the angular momentum vectors. For orbital motion, the relation is

$$\mu_m = -g_L L \quad (Eq. 1.9.5)$$

whereas that for the spinning is

$$\mu_m = -(2g_S S) \quad (Eq. 1.10.6)$$

Thus, an electron with total angular momentum quantum number  $J$  with an orientation given by  $m_J$  does not have an energy given simply by  $m_J \mu_B B$ . In fact, the energy can be expressed as

$$V = m_J (g_J \mu_B B) \quad (1.10.16)$$

where  $g_J$  is the Lande  $g$ -factor which takes into account the off-axis alignment of the total angular momentum and the total magnetic moment and is given by

$$g_J = 1 + \left\{ \frac{J(J+1) - l(l+1) + s(s+1)}{2J(J+1)} \right\} \quad (1.10.17)$$

<sup>†</sup> This series is known as Clebsch-Gordan series.

Equation (1.10.17) is reduced to Eqs (1.9.5) and (1.10.6) in the two extreme isolated cases. Thus, we have

- (i)  $g_J = 1$ , when  $s = 0$  and  $J = l$ —a value used while dealing with the orbital motion only (Eq. 1.9.5).
- (ii)  $g_J = 2$ , when  $l = 0$  and  $J = s$ —a value used while dealing only with the spin of the electron (Eq. 1.10.6).

The modification of potential energy of an electron in the framework of spin-orbit coupling is as follows.

**For 1s orbital** Here  $l = 0$  and  $s = 1/2$ . Thus  $J = 1/2$  and the Lande  $g$ -factor = 2. The potential energies of the electron in the presence of a magnetic field are

$$V''_{+1/2} = (1/2) (2\mu_B B) = \mu_B B \quad (1.10.18)$$

$$\text{and} \quad V''_{-1/2} = -(1/2) (2\mu_B B) = -\mu_B B \quad (1.10.19)$$

Thus, the energy of 1s orbital splits into two in the presence of a magnetic field.

**For 2p orbitals** Here  $l = 1$  and  $s = 1/2$ . For  $J_{\max} = 3/2$ , the permitted values of  $m_J$  are  $3/2, 1/2, -1/2$  and  $-3/2$ .

The Lande  $g$ -factor for  $J_{\max}$  is given by

$$g_J = 1 + \left[ \frac{\frac{3}{2} \left( \frac{5}{2} \right) - 1(2) + \frac{1}{2} \left( \frac{3}{2} \right)}{2 \left( \frac{3}{2} \right) \left( \frac{5}{2} \right)} \right] = 1 + \frac{1}{3} = \frac{4}{3}$$

The three degenerate 2p orbitals split into four of the following energies.

$$V_{3/2} = (3/2) (4/3) \mu_B B \quad (1.10.20)$$

$$V_{1/2} = (1/2) (4/3) \mu_B B \quad (1.10.21)$$

$$V_{-1/2} = (-1/2) (4/3) \mu_B B \quad (1.10.22)$$

$$\text{and} \quad V_{-3/2} = (-3/2) (4/3) \mu_B B \quad (1.10.23)$$

The selection rules for the spectral transition in the framework of spin-orbit coupling are

$$\Delta m_J = 0, \pm 1 \quad (1.10.24)$$

Following the above rules, six spectral transitions between 1s and 2p orbitals are possible. These are described in Table 1.10.2.

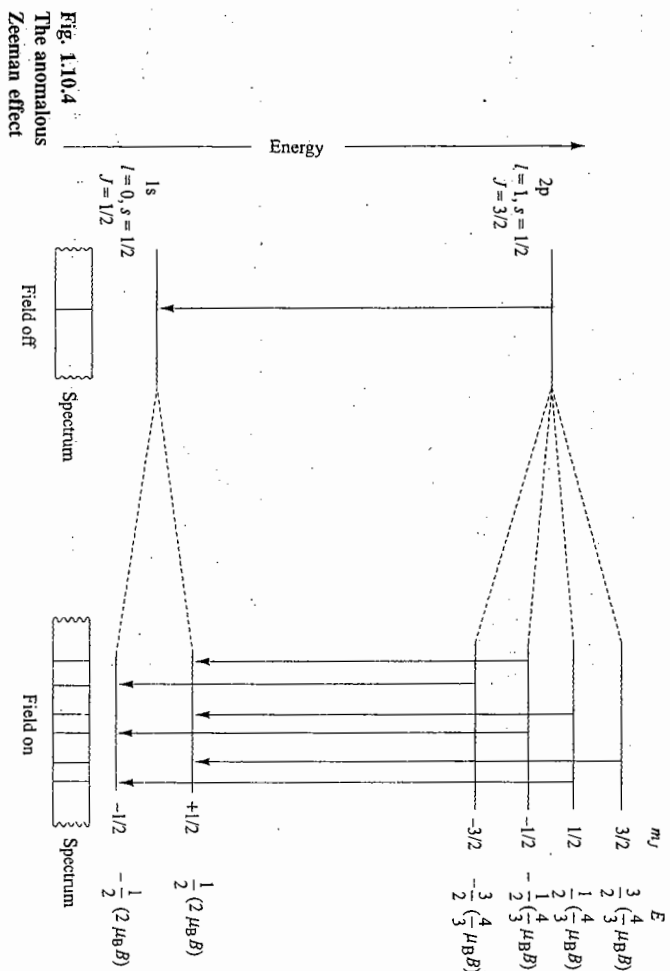
These transitions are shown in Fig. 1.10.4.

In the presence of a very strong field, the orbital and the spin magnetic moments are uncoupled and precess separately around their own axes. In such cases, the anomalous Zeeman effect is reverted to the normal Zeeman effect with the spin playing no role. This reversion is called the Paschen-Back effect.

### Paschen-Back Effect

Table 1.10.2 Spectral Transitions in the Framework of Spin-Orbit Coupling

Transition	Energy
(1) $V'_{-1/2} \rightarrow V''_{+1/2}$	$\Delta V_1 = - (5/3) \mu_B B$
(2) $V'_{-3/2} \rightarrow V''_{-1/2}$	$\Delta V_2 = - \mu_B B$
(3) $V'_{1/2} \rightarrow V''_{1/2}$	$\Delta V_3 = - (1/3) \mu_B B$
(4) $V'_{-1/2} \rightarrow V''_{-1/2}$	$\Delta V_4 = + (1/3) \mu_B B$
(5) $V'_{3/2} \rightarrow V''_{1/2}$	$\Delta V_5 = + \mu_B B$
(6) $V'_{+1/2} \rightarrow V''_{+1/2}$	$\Delta V_6 = + (5/3) \mu_B B$

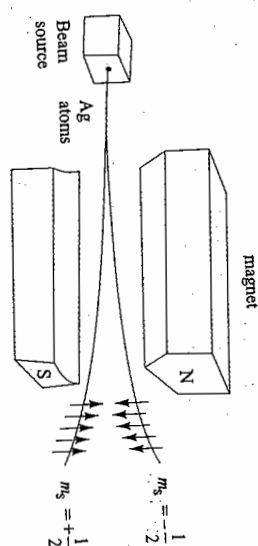


### Double Lines in the Spectra of Alkali Metals

The existence of double lines instead of one in the spectra of alkali metals can be explained on the basis of spin-orbit coupling. Take, for example, the characteristic yellow line at 589 nm emission from sodium vapour when the latter is excited by an electric discharge. This line is actually composed of two closely spaced lines, one at 589.76 nm and the other at 589.16 nm. In the ground state of sodium, the outer electron is in the s orbital and thus  $J'' = 1/2$ . When this electron occupies the next higher p orbital, the permitted values of  $J'$  are  $3/2$  and  $1/2$ . The energy

### The Stern-Gerlach Experiment

Fig. 1.10.5 Stern-Gerlach experiment



of the electron in  $J' = 3/2$  state is different from that in the  $J' = 1/2$  state. Thus, two transitions  $J' = 3/2 \rightarrow J'' = 1/2$  and  $J' = 1/2 \rightarrow J'' = 1/2$  are possible which are observed as the two closely spaced lines.

The experimental demonstration for the existence of the electron spin is due to Stern and Gerlach. They passed a beam of silver atoms through a strong inhomogeneous magnetic field and found that the beam splits symmetrically in two as shown in Fig. 1.10.5.

### 1.11 MANY-ELECTRON ATOMS

#### Expression of Hamiltonian Operator

The Hamiltonian operator for electrons in many-electron atoms can be written as

$$H_{op} = -\frac{\hbar^2}{8\pi^2 m} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \frac{Ze^2}{(4\pi\epsilon_0)r_i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{e^2}{(4\pi\epsilon_0)r_{ij}} \quad (1.11.1)$$

The first term represents the total kinetic energy of all the  $n$  electrons, the second term represents the nuclear-electronic attractions and the last term represents the electronic-electronic repulsions.

The Schrödinger equation as usual can be written as

$$H_{op} \psi = E \psi \quad (1.11.2)$$

where the function  $\psi$  is a function of  $3n$  independent variables.

Unfortunately, it has not been possible to solve Eq. (1.11.2) accurately and one has to resort to the approximate methods. The major difficulty in solving

Obviously, this splitting must be due to two specific interactions between the magnetic moment possessed by the silver atom and the external magnetic field. The silver atom has a single s-electron outside a closed shell. The fact that for a closed shell, the total orbital and spin magnetic moments are zero indicates that the outer s-electron must have only two values of magnetic moments. The latter can arise only when the electron is spinning around its own axis. Moreover, the magnitude of the splitting is found to follow Eq. (1.10.6), i.e.

$$\mu_m = -2gS$$

where  $g$  is equal to  $e/2m_e$  in SI units.



Eq. (1.11.2) comes from the electronic-electronic repulsion terms. In the absence of these terms, Schrödinger equation can be solved by writing the wave function  $\psi$  as the product of one electron wave functions (represented hereafter as  $\psi^o$ ). The latter can be chosen from the hydrogen-like wave functions. When this product function is substituted in Eq. (1.11.2), the latter splits into a number of equations, each involving the coordinates of the individual electron. The form of the resultant equations is identical to that of the hydrogen-like species. The total energy is equal to the sum of the individual energies of various electrons.

The above results are very approximate and do not represent the quantitative behaviour of electrons in the atom. However, the results can be improved by following either the *perturbation method* or the *variational method*.

In the perturbation method,<sup>†</sup> the electronic repulsion terms are considered as small perturbations on the Hamiltonian operator which neglects the electronic-electronic repulsion terms, i.e.

$$H_{\text{op}}^o = -\frac{h^2}{8\pi^2m} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \frac{Ze^2}{(4\pi\epsilon_0)r_i} \quad (1.11.3)$$

$$H_{\text{op}} = H_{\text{op}}^o + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{e^2}{(4\pi\epsilon_0)r_{ij}} \quad (1.11.4)$$

Assuming that these small perturbations do not change the wave function  $\psi^o$  very much (wave function of the given state excluding the repulsion terms), we can calculate an approximate average value of energy by employing the expectation expression

$$E = \frac{\int \psi^{o*} H_{\text{op}} \psi^o d\tau}{\int \psi^{o*} \psi^o d\tau} \quad (1.11.5)$$

(Note that the function  $\psi^o$  is not an eigenfunction of the operator  $H_{\text{op}}$  and, therefore, the operation of  $H_{\text{op}}$  on  $\psi^o$  will not yield the exact energy eigenvalue.)

Equation (1.11.5) can be written as

$$\begin{aligned} \bar{E} &= \frac{\int \psi^{o*} H_{\text{op}}^o \psi^o d\tau + \int \psi^{o*} \left( \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{e^2}{(4\pi\epsilon_0)r_{ij}} \right) \psi^o d\tau}{\int \psi^{o*} \psi^o d\tau} \\ \text{or } \bar{E} &= E^o + \frac{\int \psi^{o*} \left( \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{e^2}{(4\pi\epsilon_0)r_{ij}} \right) \psi^o d\tau}{\int \psi^{o*} \psi^o d\tau} \end{aligned} \quad (1.11.6)$$

<sup>†</sup> See Annexure X for the detail.

## The Variational Method

The second term of Eq. (1.11.6) is evaluated and adding this to  $E^o$  gives the modified approximate value of the energy of the system. For example, in case of helium atom which contains two electrons ( $n = 2$ ) and has two positive charges at the nucleus ( $Z = 2$ ), the value of second term is found to be  $5e^2/[(4\pi\epsilon_0)(4a_0)]$ . Now since  $E_H = -e^2/(4\pi\epsilon_0)(2a_0)$  the value of the second term is equal to  $-(5/2)E_H$ , i.e.  $-(5/2)(-13.6 \text{ eV}) = 34.0 \text{ eV}$ . Thus

$$\bar{E} = E^o + 34.0 \text{ eV}$$

The numerical value of  $E^o$  is

$$E^o = E_1^o + E_2^o = \frac{Z^2 E_H}{n_1^2} + \frac{Z^2 E_H}{n_2^2} = \frac{4E_H}{n_1^2} + \frac{4E_H}{n_2^2}$$

For the helium atom in the ground state, both  $n_1$  and  $n_2$  are equal to one, thus

$$E^o = 8 E_H = 8 (-13.6 \text{ eV}) = -108.8 \text{ eV}$$

and hence

$$E = -108.8 \text{ eV} + 34.0 \text{ eV} = -74.8 \text{ eV}$$

The experimental value is  $-79.0 \text{ eV}$ .

In the variational method, the wave function is written containing a few adjustable parameters. For example, in the hydrogen-like orbitals, the nuclear charge  $Z$  may be taken as the adjustable parameter. This will take into account what is known as the effective screening of the positive nuclear charge. For example, in the helium atom, the negative charge cloud of the first electron results in an effective screening of the positive nuclear charges at the nucleus but sees a charge which is a little bit less than two. The same is also true for the first electron. The best choice of wave functions so far widely used is due to *Slater* and thus are known as the *Slater-orbitals*. The latter have angular distributions identical to those of hydrogen-like orbitals but the radial distribution functions are given by the following expression.

$$R_{\text{Slater}} = \left( \frac{2\zeta}{a_0} \right)^{n+1/2} \left[ \frac{1}{(2n)!} \right] r^{n-1} e^{-\zeta r/a_0} \quad (1.11.7)$$

where the parameter  $\zeta$  is called the orbital exponent.

The variation method is based on the *variational theorem*<sup>†</sup> which may be stated as follows.

If one employs a well behaved approximate wave function in evaluating the expectation value by using the expression

$$\bar{E} = \frac{\int \psi^* H_{\text{op}} \psi d\tau}{\int \psi^* \psi d\tau} \quad (1.11.8)$$

then the value of  $\bar{E}$  so obtained will always be algebraically equal to or greater than the true energy  $E_0$  of the system, i.e.  $\bar{E} \geq E_0$ .

<sup>†</sup> See Annexure XII for the proof of variational theorem.

In Eq. (1.11.8), the Hamiltonian operator  $H_{op}$  is the complete and correct operator of the system under study.

Now the energy  $\tilde{E}$  can be written in terms of adjustable parameters. The best choice of the values of adjustable parameters can be obtained by minimizing the value of  $\tilde{E}$ , i.e. which brings  $\tilde{E}$  as close as possible to the true energy of the system. This can be done by taking the first derivative of  $\tilde{E}$  with respect to the adjustable parameter and equating the resultant expression to zero. Take, for example, the helium atom, the trial function could be chosen from the hydrogen-like orbitals by replacing  $Z$  by  $Z'$ , i.e.

$$\psi = \psi_{1s}(1) \psi_{1s}(2) = \left(\frac{1}{\pi}\right) \left(\frac{Z'}{a_0}\right)^3 \exp(-Z'r_1/a_0) \exp(-Z'r_2/a_0)$$

$$\text{Now } H_{op} = -\frac{\hbar^2}{8\pi^2 m} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{(4\pi\epsilon_0)r_1} - \frac{Ze^2}{(4\pi\epsilon_0)r_2} + \frac{e^2}{(4\pi\epsilon_0)r_{12}}$$

$$\text{and } \tilde{E} = \int \psi^* H_{op} \psi d\tau = \left[ -2Z'^2 + \frac{27}{4} Z' \right] E_H$$

$$\text{Now } \left( \frac{\partial \tilde{E}}{\partial Z'} \right) = \left( -4Z' + \frac{27}{4} \right) E_H = 0$$

and hence

$$Z' = \frac{27}{16}$$

Thus, the approximate energy  $\tilde{E}$  becomes

$$\begin{aligned} \tilde{E} &= \left[ -2 \left( \frac{27}{16} \right)^2 + \left( \frac{27}{4} \right) \left( \frac{27}{16} \right) \right] E_H \\ &= 5.70 E_H = 5.70 (-13.6 \text{ eV}) = -77.5 \text{ eV} \end{aligned}$$

This is to be compared with the experimental value of  $-79.0 \text{ eV}$ †

## Self-Consistent Field Method

The above procedure of solving the Schrödinger equation cannot be extended if the atom contains larger number of electrons. Another method, which is a more practical one, was suggested by Hartree in 1928 and is known as the self-consistent field (SCF) method. In this method, we have

1. The total wave function of the system can be written as the product of one-electron wave functions, i.e.

$$\psi = \phi_1(1) \phi_2(2) \phi_3(3) \dots \phi_n(n)$$

where  $\phi_i(1)$  is the wave function of the electron 1, and so on. These one-electron wave functions can be any trial functions.

† See Annexure XII for the details.

2. Each electron is supposed to be moving in an average spherically symmetric potential energy function  $V_i$  arises because of the nuclear attraction and the repulsion from all other electrons. In order to evaluate the function  $V_i$  for the  $i$ th electron, which is usually done by numerical integration, we require the knowledge of the wave functions of all electrons except the one under study.

3. Once the function  $V_i$  is available, we can write the one-electron Schrödinger equation as

$$-\frac{\hbar^2}{8\pi^2 m} \nabla_i^2 \phi_i + V_i \phi_i = E_i \phi_i \quad (1.11.9)$$

Solving this equation, we get the improved wave function  $\phi_i$  and the corresponding energy  $E_i$ .

Now, we can summarize the procedural part of the SCF-method. Suppose, we start with the electron-1. First of all  $V_1$  is evaluated by employing the trial functions  $\phi_2(2), \phi_3(3), \dots, \phi_n(n)$ . This is substituted in Eq. (1.11.9) and is solved for the first-improved wave function  $\phi_1'(1)$  and the corresponding energy  $E_1'$ . We now shift to the electron-2 and evaluate the function  $V_2$  by employing the first-improved wave function  $\phi_1'(1)$  and the starting trial-functions  $\phi_3(3), \phi_4(4), \dots, \phi_n(n)$ . This is substituted in Eq. (1.11.9) and is solved for the first-improved wave function  $\phi_2'(2)$  and the corresponding energy  $E_2'$ . This process is repeated one by one for all the electrons and thus we get the first-improved wave functions and the corresponding first-improved energies. Now, we start once again from the electron-1. Its modified potential  $V_1$  is evaluated by employing the first-improved wave functions of all other electrons, viz.,  $\phi_2'(2), \phi_3'(3), \dots$ . On substituting  $V_1$  in Eq. (1.11.9) and subsequently solving, we get the second-improved wave function  $\phi_1''(1)$  and the corresponding energy  $E_1''$ . Similarly, the second-improved wave functions for all the  $n$ -electrons are obtained one by one. We then again repeat the process third time, this time using the second-improved  $\phi$  functions and thus obtain the third-improved wave functions and third-improved energies. This iterative process is repeated until the  $n$ th-improved wave functions agree within the limit with the  $(n-1)$ th-improved wave functions, i.e. they become self-consistent. The energy of the atom is then given by

$$\tilde{E} = \sum_{i=1}^n \tilde{E}_i \quad (1.11.10)$$

The Schrödinger equation as given by Eq. (1.11.9) for the multi-electron atom is identical to that of a single electron in the hydrogen-like species, with the only difference of the form of the spherically symmetric potential-energy term  $V_i$ . Thus, the mechanism of solution of Eq. (1.11.9) is very similar to that employed for the hydrogen-like species. Since  $V_i$  appears only in the radial equations, the solution for the angular dependence  $\Theta(\theta)$  and  $\Phi(\phi)$  are exactly the same as those of hydrogen-like species. This means that the angular shapes and probability distributions in the multi-electron atoms are exactly identical to those for the single

electron in the hydrogen-like species. Thus the various orbitals may be designated as usual by the symbol  $s$ ,  $p$ ,  $d$  and  $f$  and so on.

The SCF method simply provides the radial distribution of individual electrons in the atom. Moreover, these distributions are obtained numerically in the form of tables or plots rather than as the explicit equations as is in the case of hydrogen-like species. This radial distribution again depends on the two quantum numbers, viz.,  $n$  and  $l$ . The energy associated with any radial distribution also depends on these two quantum numbers unlike the case of hydrogen-like species where the energy depends only on the principal quantum number  $n$ . The total wave function of the electron can be obtained as usual by multiplying its radial distribution with those of angular distribution. As stated earlier, the latter are identical to those for the hydrogen-like species.

Each electron will be described by the total wave function and hence by an orbital. The latter, as usual, is designated by the three quantum numbers  $n$ ,  $l$  and  $m$ . The principal quantum number  $n$  represents the different shells of the atom and are represented by the scheme shown in the following.

Value of $n$	1	2	3	4	...
Symbol used for the shell	K	L	M	N	...

The quantum number  $l$  represents the total angular momentum of the electron and also the shape of the orbital. As is in the case of hydrogen-like species, the various orbitals are represented by the symbols  $s$ ,  $p$ ,  $d$ ,  $f$  depending upon the value of  $l$ . The quantum number  $m$  represents the  $z$ -component of the angular momentum and also the orientation of the orbital.

As usual, the principal quantum number  $n$  is the most important in deciding the energy of the orbital. The actual energy of any particular orbital also depends on the value of  $l$ . For example, the energy of  $2p$ -electron is higher than the  $2s$ -electron. In third quantum shell, the increasing order of energy is  $3s < 3p < 3d$ . In general, the energy increases as the value of  $l$  increases within the same shell. This can be explained on the basis of radial distribution. The electron with a larger value of  $l$  virtually spends its time relatively far from the nucleus as compared to that for the smaller value of  $l$ . Thus, the former experiences lesser attraction by the nucleus and hence its energy is larger. However, it may be noted down that the energy of an orbital does not depend upon the value of  $m$ . Thus, different orbitals with the same value of  $l$  but different values of  $m$  are degenerate in nature, i.e. their energies are identical.

Show that the electron distribution in the ground state of the neon atom has spherical symmetry.

The term spherical symmetry means the overall distribution of electrons is independent of the angles  $\theta$  and  $\varphi$ . In the present case, the overall probability distribution will be given as  $(p_x^2 + p_y^2 + p_z^2)$ .

The angular expressions of  $p_x$ ,  $p_y$  and  $p_z$  are

$$p_x = \left( \frac{\sqrt{3}}{2} \sin \theta \right) \left( \frac{1}{\sqrt{\pi}} \cos \varphi \right)$$

$$p_y = \left( \frac{\sqrt{3}}{2} \sin \theta \right) \left( \frac{1}{\sqrt{\pi}} \sin \varphi \right)$$

$$p_z = \left( \frac{\sqrt{6}}{2} \cos \theta \right) \left( \frac{1}{\sqrt{2\pi}} \right)$$

$$\begin{aligned} \text{Thus, } p_x^2 + p_y^2 + p_z^2 &= \frac{3}{4\pi} \sin^2 \theta \cos^2 \varphi + \frac{3}{4\pi} \sin^2 \theta \sin^2 \varphi + \frac{3}{4\pi} \cos^2 \theta \\ &= \frac{3}{4\pi} \sin^2 \theta (\cos^2 \varphi + \sin^2 \varphi) + \frac{3}{4\pi} \cos^2 \theta \\ &= \frac{3}{4\pi} (\sin^2 \theta + \cos^2 \theta) = \frac{3}{4\pi} \end{aligned}$$

Since  $p_x^2 + p_y^2 + p_z^2$  is independent of angles  $\theta$  and  $\varphi$ , the ground state of the neon atom is spherically symmetrical.

[In general, the sum of the probability distribution functions for a given value of the azimuthal quantum number  $l$  and all the values of the magnetic quantum number  $m$  is independent of angles  $\theta$  and  $\varphi$  and is equal to  $(2l + 1)/4\pi$ . Such configurations are thus spherically symmetrical.]

## 1.12 THE INDISTINGUISHABILITY OF ELECTRONS AND THE PAULI EXCLUSION PRINCIPLE

Let the total wave function of a system containing two electrons be written as the product of one-electron spatial wave functions  $\varphi_1$  and  $\varphi_2$ . We can write this as

$$\psi_{12} = \varphi_1(1)\varphi_2(2) \quad (1.12.1)$$

where  $\varphi_1$  and  $\varphi_2$  are occupied by the electrons 1 and 2, respectively. However, we can equally write another product function where  $\varphi_1$  is occupied by the electron 2 and  $\varphi_2$  by the electron 1, i.e.

$$\psi_{21} = \varphi_1(2)\varphi_2(1) \quad (1.12.2)$$

This follows from the fact that the two electrons are indistinguishable in the system and thus we cannot precisely label the individual electrons. The functions  $\psi_{12}$  and  $\psi_{21}$  taken separately do not meet the requirement of indistinguishability of the electron. However, if we take the linear combination of these two functions, we can construct a wave function which besides being the solution of the appropriate Schrödinger equation also satisfies the indistinguishability requirement. Moreover, the resultant linear combination should represent the same probability distribution as those represented by functions  $\psi_{12}$  or  $\psi_{21}$ . This means that the square of the

### Problem 1.11.1

#### Solution

resultant wave function should be equal to the square of either of the functions  $\psi_{12}$  and  $\psi_{21}$ . The two such combinations are

$$\psi_s = \frac{1}{\sqrt{2}} (\psi_{12} + \psi_{21}) = \frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) + \phi_1(2)\phi_2(1)] \quad (1.12.3)$$

$$\text{and } \psi_a = \frac{1}{\sqrt{2}} (\psi_{12} - \psi_{21}) = \frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)] \quad (1.12.4)$$

The subscripts 's' and 'a' stand for symmetric and antisymmetric, respectively. The function  $\psi_s$  remains symmetric on interchanging the two electrons whereas the function  $\psi_a$  becomes  $-\psi_a$  on interchanging the two electrons.

### Spin Wave Functions for a Two-Electron System

The electron in an atom is associated with the spin and thus the electron must also be indistinguishable with respect to the orientation of intrinsic spin. We represent the spin of the electron by the spin functions. It is customary to write the spin with  $m_s = +1/2$  by the spin function which is written as  $\alpha$  and that with  $m_s = -1/2$  with another function written as  $\beta$ . Experimentally, it is possible to determine the total spin angular momentum of a system and not the spin of the individual electrons. Thus, we cannot state that any particular electron has spin  $\alpha$  (or  $\beta$ ). Say, for example, in the above system the two electrons have opposite spins, one is having  $\alpha$ -spin (not known whether the electron 1 or electron 2) and the other is having  $\beta$ -spin. Thus, we cannot say that the electron 1 has a  $\alpha$ -spin and the electron 2 has a  $\beta$ -spin. It is equally probable that the electron 2 has a  $\alpha$ -spin and the electron 1 has a  $\beta$ -spin. A complete description of the electron can be described with the help of spin orbital which is simply the product of spatial and spin functions. Thus, an electron in  $\phi_1$  can be written as  $\phi_1\alpha$  or  $\phi_1\beta$  depending upon the spin of the electron.

### Total Wave Function for a Two-Electron System

If the interaction between spin and orbital motion is neglected, the total wave function of the system can be represented by the product of total spatial function and the total spin function. For the two electrons, the total spin functions consistent with the indistinguishability condition are

$$\alpha(1)\alpha(2) \quad (1.12.5)$$

$$\beta(1)\beta(2) \quad (1.12.6)$$

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (1.12.7)$$

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (1.12.8)$$

The first three functions are symmetric in nature and the last one is antisymmetric in nature. Thus, interchanging of two electrons reproduces the first three functions while the fourth one reverses the sign.

Now, when these four spin functions are combined with the two spatial functions  $\psi_s$  and  $\psi_a$ , we get eight different combinations as shown below.

$$\frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) + \phi_1(2)\phi_2(1)] [\alpha(1)\alpha(2)] \quad (\text{symmetric})$$

$$\frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) + \phi_1(2)\phi_2(1)] [\beta(1)\beta(2)] \quad (\text{symmetric})$$

$$\frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) + \phi_1(2)\phi_2(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (\text{symmetric})$$

$$\frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) + \phi_1(2)\phi_2(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (\text{antisymmetric})$$

$$\frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)] [\alpha(1)\alpha(2)] \quad (\text{antisymmetric})$$

$$\frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)] [\beta(1)\beta(2)] \quad (\text{antisymmetric})$$

$$\frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (\text{antisymmetric})$$

$$\frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (\text{symmetric})$$

### Acceptable Wave Functions

The behaviour of the electron in an atom as suggested by the experimental evidences requires that the total wavefunction for a system of electrons must be *antisymmetric* to the simultaneous exchange of coordinates and spins between any pair of electrons. Thus, out of the above eight functions, only four antisymmetric functions represent the realistic behaviour of electrons. These are:

$$\frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) + \phi_1(2)\phi_2(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (1.12.9)$$

$$\frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)] [\alpha(1)\alpha(2)] \quad (1.12.10)$$

$$\frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)] [\beta(1)\beta(2)] \quad (1.12.11)$$

$$\frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (1.12.12)$$

### Pauli Exclusion Principle

The above criterion of antisymmetric nature was first enunciated by Wolfgang Pauli and thus is known as the *Pauli exclusion principle*. It may be mentioned here that the above antisymmetric principle is followed by all those particles which have a

half-integral spin (i.e.  $s = 1/2$ ) such as electrons, protons and neutrons. The various nuclei, atoms, ions and molecules with an odd number of electrons, protons and neutrons also have a half-integral spin and thus follow the above antisymmetric principle. Such particles are known as *fermions* (after Enrico Fermi) and they follow the Fermi-Dirac statistics. On the other hand, the various particles with integral spin follow the symmetric principle (i.e. their functions are symmetric on interchanging the particles) and are known as *bosons* (after Satyendra Nath Bose). Such particles follow Bose-Einstein statistics. Examples include photons and atoms, ions, nuclei, and molecules with an even number of electrons, protons and neutrons.

### A More Familiar Form of Pauli Exclusion Principle

Take, for example, the case in which both the spatial orbitals are identical, say  $1s$  orbital. The two electrons thus have the same quantum numbers  $n$ ,  $l$  and  $m$ . Substituting  $1s$  in place of both  $\varphi_1$  and  $\varphi_2$  in Eqs (1.12.9) to (1.12.12), we get

$$\frac{1}{\sqrt{2}} [1s(1)1s(2) + 1s(2)1s(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (1.12.13)$$

$$\frac{1}{\sqrt{2}} [1s(1)1s(2) - 1s(2)1s(1)] [\alpha(1)\alpha(2)] \quad (1.12.14)$$

$$\frac{1}{\sqrt{2}} [1s(1)1s(2) - 1s(2)1s(1)] [\beta(1)\beta(2)] \quad (1.12.15)$$

$$\frac{1}{\sqrt{2}} [1s(1)1s(2) - 1s(2)1s(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (1.12.16)$$

Equations (1.12.14) to (1.12.16) are equal to zero, and hence we are left with only one function in which the spin of the two electrons are different, i.e. the value of the fourth quantum number is different for the two electrons. This leads to a more familiar form of Pauli exclusion principle stated as follows.

*No two electrons in a given atom may have all the four quantum numbers the same.*

When the two spatial orbitals are different, the value of at least one of the quantum number  $n$ ,  $l$  and  $m$  is different and thus the two electrons may have either the same or different spins.

### Number of Electrons in an Orbital

Pauli exclusion principle involves the restriction on the number of electrons that can be accommodated in one orbital. Taking an example of feeding the electrons in  $1s$  orbital one by one, we find that for the first electron, the four quantum numbers are  $n = 1$ ,  $l = 0$ ,  $m = 0$  and  $m_s = +1/2$  (or equally  $-1/2$ ). For the second electron in the same orbital, the first three quantum numbers have the same values, viz.,  $n = 1$ ,  $l = 0$  and  $m = 0$ . Now according to the Pauli exclusion principle, the fourth one (i.e. the spin quantum number) has to have a different value. Thus,  $m_s = -1/2$  (or  $+1/2$  if the first electron has a value of  $-1/2$ ). Now, if we feed the third electron, we will have spin quantum number either equal to  $+1/2$  or  $-1/2$  and thus all the four quantum numbers of this electron are identical to those of either the first electron. This is in violation with the Pauli principle and thus we cannot have more than two electrons in the same orbital.

The presence of two electrons in the same orbital with the opposite spins gives rise to the more stable configuration from the energetic viewpoint. The two electrons

are present in the same region of the space and thus it is expected that there occurs maximum electron-electron repulsion interaction. But because of the opposite spins, the two tiny magnets generated because of the spinning of electrons have unlike poles near to each other, i.e. the north pole of the one of the magnets is near to the south pole of the other and vice versa. This gives rise to the most stable interaction with each other.

The antisymmetric two-electron wave function as given by Eq. (1.12.13) can be opened to give

$$\begin{aligned} \psi &= \frac{1}{\sqrt{2}} [1s(1)1s(2) + 1s(2)1s(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\ &= \frac{1}{2} [1s(1)1s(2)\alpha(1)\beta(2) - 1s(1)1s(2)\alpha(2)\beta(1) \\ &\quad + 1s(2)1s(1)\alpha(1)\beta(2) - 1s(2)1s(1)\alpha(2)\beta(1)] \\ &= 1s(1)\alpha(1)1s(2)\beta(2) - 1s(1)\beta(1)1s(2)\alpha(2) \end{aligned}$$

The above expression can be written in a determinant form as

$$\psi = \frac{|1s(1)\alpha(1) \quad 1s(1)\beta(1)|}{|1s(2)\alpha(2) \quad 1s(2)\beta(2)|} \quad \text{or simply as} \quad \psi = \frac{|1s(1) \quad 1s(1)|}{|1s(2) \quad 1s(2)|} \quad (1.12.17)$$

where the spatial function without overhead bar represents  $\alpha$ -spin and that with any overhead bar represents  $\beta$ -spin. The Pauli exclusion principle is automatically explained by the properties of a determinant. If two electrons are placed into the same spin orbital, then two columns of the determinant become identical, hence the wave function becomes zero. The antisymmetric nature of the wave function  $\psi$  on interchanging the coordinates and spins between any pair of electrons is also satisfied by the determinant form of the wave function. Exchanging the indices of two electrons in the determinant form of wave function is equivalent to interchanging of two rows of the determinant, which changes sign as a consequence. There is another property which may be highlighted here. If a row (or column) of a determinant is replaced by the linear combination of this row (or column) with other rows (or columns), the value of determinant remains unchanged. A similar replacement involving spin orbitals in the determinant form of the wave function does not cause any change in the overall wave function.

The determinant form of writing a wave function can be easily extended to a system containing more than two electrons. In the determinant form, columns represent different spin orbitals (each of which is product of spatial wave function and spin wave function) and the electrons to the wave functions are assigned row-wise. For example, for Li atom, we can write

$$\psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

where the factor  $1/\sqrt{3!}$  represents the normalization constant of the wave function  $\psi$ .

*Note:* For atoms with closed-shell configuration (e.g. He, Be, Ne) only one Slater determinant can be written, while for atoms with open-shell configurations (e.g. Li, B, C) more than one Slater determinant is possible and the total wave function is represented as linear combination of these determinants.

## 1.13 ATOMIC TERM SYMBOLS

The electronic configuration of a lighter element (atomic number less than 46) is designated by the atomic term symbol. This provides information regarding the total orbital angular momentum quantum number (symbol:  $L$ ). The symbols used for the quantum number  $L$  are as follows.

Value of $L$ :	0	1	2	3	4	5	...
Symbol :	S	P	D	F	G	H	...

These symbols correspond to the letter s, p, d, f, g, ... used to represent the orbital angular quantum number  $l = 0, 1, 2, 3, 4, \dots$ , respectively.

The symbol is also left superscripted and right subscripted which, respectively, represent the spin multiplicity ( $= 2S + 1$ , where  $S$  is the total spin angular momentum quantum number) and the total angular momentum quantum number (symbol:  $J$ ) of the electronic configuration. A few examples are  $^1S_0$ ,  $^3S_0$ ,  $^1D_2$ ,  $^3P_0$ ,  $^3P_1$ ,  $^3P_2$  and so on.

For lighter elements, the total angular momentum is determined by using the scheme of Russell-Saunders coupling, also known as spin-orbit coupling.<sup>†</sup> This scheme is based on the fact that both the total orbital angular momentum and the total spin angular momentum are separately conserved, and thus both these quantities may be determined separately by the vector additions of individual orbital and spin angular momenta by using the expressions

$$L_{\text{total}} = \sum_i L_i \quad \text{and} \quad S_{\text{total}} = \sum_i S_i$$

These two quantities are then coupled to give the total angular momentum (symbol:  $J$ )

$$J = L_{\text{total}} + S_{\text{total}}$$

The physical quantities  $L_{\text{total}}$  and  $S_{\text{total}}$  are characterised by the quantum number  $L$  and  $S$ , respectively. The values of these numbers are conveniently assigned from the knowledge of the quantum numbers  $M_l$  and  $M_s$  which, respectively, represent the  $z$ -components of the total orbital angular momentum and the total spin angular momentum. Since the  $z$ -components of orbital (or spin) angular momentum act along the same axis, the  $z$ -components of the total orbital (or spin) angular momentum is obtained by the scalar addition of  $z$ -component of individual orbital (or spin) angular momentum, i.e.

$$L_{z,\text{total}} = \sum_i L_{z,i} = \left( \sum_i m_l \right) (h/2\pi) = M_l (h/2\pi)$$

$$S_{z,\text{total}} = \sum_i S_{z,i} = \left( \sum_i m_s \right) (h/2\pi) = M_s (h/2\pi)$$

<sup>†</sup> For atoms with atomic number greater than 46, the total orbital (or spin) angular momentum is no longer conserved, but the individual total angular momentum  $J = L + S$  is conserved. The total angular momentum in this case is evaluated by the expression  $J = \sum_i J_i$ . This scheme is called  $jj$  coupling.

## A Few Facts about Angular

## Momentum

## Quantum Numbers

The  $z$ -component of total angular momentum is given by

$$J_z = L_{z,\text{total}} + S_{z,\text{total}} = (M_l + M_s) (h/2\pi) = M_J (h/2\pi)$$

- For a given value of  $L$ , the associated allowed values of  $M_l$  are  $2L + 1$ , which have the values of

$$L, L - 1, \dots, -(L - 1), -L$$

- For a given value of  $S$ , the associated allowed values of  $M_s$  are  $2S + 1$ , which have the values of

$$S, S - 1, \dots, -(S - 1), -S$$

- For a given value of  $J$ , the associated allowed values of  $M_J$  are  $2J + 1$ , which have the values of

$$J, J - 1, \dots, -(J - 1), -J$$

- The quantum number  $J$  has a maximum value when both  $L$  and  $S$  point in the same direction. Thus, the maximum value of  $J$  is  $L + S$ .

- The quantum number  $J$  has a minimum value when  $L$  and  $S$  point in the opposite directions. Thus, the minimum value of  $J$  is  $L - S$ .

- The total allowed values of  $J$  are given by

$$J_{\text{max}}, J_{\text{max}} - 1, \dots, J_{\text{min}} \\ \text{i.e.} \quad L + S, L + S - 1, \dots, |L - S|$$

- Atomic states arising from the same electronic configuration and having the same value of  $L$  and  $S$  are said to belong to the same term.

- States belonging to different terms have different energies, since the interelectronic repulsion is different for each term.

Term Symbol for ( $ns$ )<sup>2</sup> Configuration

The two electrons are said to be equivalent electrons as they have the same values of  $n$  and  $l$ . We write the configuration ( $ns$ )<sup>2</sup> as  $ns \bar{ns}$ , where  $ns$  represents spin orbital occupied by electron having  $\alpha$ -spin and  $\bar{ns}$  represents spin orbital occupied by electron having  $\beta$ -spin. Diagrammatically, this configuration may be represented as follows.

Orbital

	$ns$	$\bar{ns}$
Value of $m_l$	$\boxed{\uparrow}$	$\boxed{\downarrow}$
Value of $m_s$	0	0
	+1/2	-1/2

For this configuration, we have

$$M_l = m_{l1} + m_{l2} = 0 + 0 = 0$$

$$M_s = m_{s1} + m_{s2} = +1/2 - 1/2 = 0$$

The value of  $M_l$  equal to zero implies that  $L = 0$ .

The value of  $M_s$  equal to zero implies that  $S = 0$ .

The spin multiplicity,  $2S + 1 = 2 \times 0 + 1 = 1$

The value of  $J = L + S = 0$

The symbol corresponding to  $L = 0$  is S. Hence, the term symbol for the configuration  $ns^2$  is  $^1S_0$ .



### Term Symbol for $nsn's$ Configuration

The two electrons are said to be nonequivalent as they have different values of  $n$ . For two electrons in two different  $s$  orbitals, there are four spin orbitals  $ns, \overline{ns}, n's$  and  $\overline{n's}$ . The configurations attained by this system along with their  $M_l$  and  $M_s$  values are described in Table 1.13.1.

Table 1.13.1 Four Configurations of  $nsn's$  System

No.	Configuration				Values of	
	$ns$ $m_l$ $m_s$	$\overline{ns}$ $0$ $-1/2$	$n's$ $0$ $+1/2$	$\overline{n's}$ $0$ $-1/2$	$M_l = \sum_i m_{l_i}$	$M_s = \sum_i m_{s_i}$
1.	$\uparrow$	$\square$	$\uparrow$	$\square$	$0 + 0 = 0$	$+\frac{1}{2} + \frac{1}{2} = +1$
2.	$\uparrow$	$\square$	$\square$	$\downarrow$	$0 + 0 = 0$	$+\frac{1}{2} - \frac{1}{2} = 0$
3.	$\square$	$\downarrow$	$\uparrow$	$\square$	$0 + 0 = 0$	$-\frac{1}{2} + \frac{1}{2} = 0$
4.	$\square$	$\downarrow$	$\square$	$\downarrow$	$0 + 0 = 0$	$-\frac{1}{2} - \frac{1}{2} = -1$

The assignment of term symbols is as follows.

- All the four configurations listed in Table 1.13.1 have  $M_l = 0$ . This implies that  $L = 0$ .

The maximum value of  $M_s$  is  $+1$ . This implies that  $S = 1$ .

The spin multiplicity,  $2S + 1 = 2 \times 1 + 1 = 3$ . These correspond to  $M_s = +1, M_s = 0$  and  $M_s = -1$ .

The symbol corresponding to  $L = 0$  is  $S$ .

Hence, the configurations 1, 2 (or 3) and 4 are assigned the term symbol  $^3S_1$ . This is called a triplet S state.

- The only left out configuration is 3 (or 2). For this configuration, we have

The value of  $M_l = 0$ . This implies that  $L = 0$ .

The value of  $M_s = 0$ . This implies that  $S = 0$ .

The spin multiplicity,  $2S + 1 = 2 \times 0 + 1 = 1$

The value of  $J = L + S = 0 + 0 = 0$

The symbol corresponding to  $L = 0$  is  $S$ . Hence, the term symbol for the configuration 3 is  $^1S_0$ . This is called a singlet S state.

To sum up, the term symbols for the electronic configuration  $nsn's$  are  $^3S_1$  and  $^1S_0$ . The values of  $M_l$  and  $M_s$  are necessarily zero for a completely filled subshell. Consequently, the configurations  $(1s)^2$  and  $(2s)^2$  need not be considered while determining the term symbols. We consider only  $(2p)^2$  electronic configuration.

### Term Symbols for $(1s)^2(2s)^2(2p)^2$ Configuration

The number of ways of assigning two electrons ( $N = 2$ ) amongst six spin orbitals ( $G = 6$ ) involving  $p$  orbitals is given by

$$\frac{G!}{N!(G-N)!} = \frac{6!}{2!4!} = 15$$

These fifteen configurations along with their values of  $M_l$  and  $M_s$  are listed in Table 1.13.2.

Table 1.13.2 Fifteen Electronic Configuration of  $(2p)^2$ 

No.	Configurations										Values of	
	$2p_{+1}$ $m_l$ $m_s$	$2p_{+1}$ $+1$ $+1/2$	$2p_0$ $0$ $+1/2$	$2p_0$ $0$ $-1/2$	$2p_{-1}$ $-1$ $+1/2$	$2p_{-1}$ $-1$ $-1/2$	$M_l = \sum_i m_{l_i}$	$M_s = \sum_i m_{s_i}$				
1.	$\uparrow$	$\downarrow$	$\square$	$\square$	$\square$	$\square$	$+1 + 1 = +2$	$+\frac{1}{2} - \frac{1}{2} = 0$				
2.	$\uparrow$	$\square$	$\uparrow$	$\square$	$\square$	$\square$	$+1 + 0 = +1$	$+\frac{1}{2} + \frac{1}{2} = +1$				
3.	$\uparrow$	$\square$	$\square$	$\downarrow$	$\square$	$\square$	$+1 + 0 = +1$	$+\frac{1}{2} - \frac{1}{2} = 0$				
4.	$\uparrow$	$\square$	$\square$	$\square$	$\uparrow$	$\square$	$+1 - 1 = 0$	$+\frac{1}{2} + \frac{1}{2} = +1$				
5.	$\uparrow$	$\square$	$\square$	$\square$	$\square$	$\downarrow$	$+1 - 1 = 0$	$+\frac{1}{2} - \frac{1}{2} = 0$				
6.	$\square$	$\downarrow$	$\uparrow$	$\square$	$\square$	$\square$	$+1 + 0 = +1$	$-\frac{1}{2} + \frac{1}{2} = 0$				
7.	$\square$	$\downarrow$	$\square$	$\downarrow$	$\square$	$\square$	$+1 + 0 = +1$	$-\frac{1}{2} - \frac{1}{2} = -1$				
8.	$\square$	$\downarrow$	$\square$	$\square$	$\uparrow$	$\square$	$+1 - 1 = 0$	$-\frac{1}{2} + \frac{1}{2} = 0$				
9.	$\square$	$\downarrow$	$\square$	$\square$	$\square$	$\downarrow$	$+1 - 1 = 0$	$-\frac{1}{2} - \frac{1}{2} = -1$				
10.	$\square$	$\square$	$\uparrow$	$\downarrow$	$\square$	$\square$	$0 + 0 = 0$	$+\frac{1}{2} - \frac{1}{2} = 0$				
11.	$\square$	$\square$	$\uparrow$	$\square$	$\uparrow$	$\square$	$0 - 1 = -1$	$+\frac{1}{2} + \frac{1}{2} = +1$				
12.	$\square$	$\square$	$\uparrow$	$\square$	$\square$	$\downarrow$	$0 - 1 = -1$	$+\frac{1}{2} - \frac{1}{2} = 0$				
13.	$\square$	$\square$	$\square$	$\downarrow$	$\uparrow$	$\square$	$0 - 1 = -1$	$-\frac{1}{2} + \frac{1}{2} = 0$				
14.	$\square$	$\square$	$\square$	$\downarrow$	$\square$	$\downarrow$	$0 - 1 = -1$	$-\frac{1}{2} - \frac{1}{2} = -1$				
15.	$\square$	$\square$	$\square$	$\square$	$\uparrow$	$\downarrow$	$-1 - 1 = -2$	$+\frac{1}{2} - \frac{1}{2} = 0$				

The assignment of term symbols is described in the following.

- The largest value of  $M_l$  is 2. This implies that  $L = 2$ .

The associated value of  $M_s$  is 0. This implies that  $S = 0$ . For  $L = 2$ ,  $M_l$  can have values +2, +1, 0, -1 and -2.

There are thus five configurations belonging to  $L = 2$  and  $S = 0$  state.

There are:

Configuration 1	$M_l = 2$	and	$M_s = 0$
Configuration 3	$M_l = 1$	and	$M_s = 0$
Configuration 5	$M_l = 0$	and	$M_s = 0$
Configuration 12	$M_l = -1$	and	$M_s = 0$
Configuration 15	$M_l = -2$	and	$M_s = 0$

For these configurations, we have

The value of spin multiplicity,  $2S + 1 = 2 \times 0 + 1 = 1$

The value of  $J = L + S = 2 + 0 = 2$

The symbol for  $L = 2$  is D.

Hence, the term symbol for the above five configurations is  $^1D_2$ .

- In the remaining 10 configurations in Table 1.13.2, the maximum value of  $M_l = +1$ . This implies that  $L = 1$ . Associated with this, the values of  $M_l$  are +1, 0 and -1. Associated with  $M_l = +1$ , the maximum value of  $M_s = +1$ . This implies that  $S = 1$ . The associated values of  $M_s$  are +1, 0 and -1.

Thus, with each of three values of  $M_l$ , there are three values of  $M_s$ . Hence, there are a total of nine configurations associated with  $L = 1$  and  $S = 1$  state. These configurations along with the values of  $M_l (= M_l + M_s)$  are as follows.

Configuration 2	$M_l = +1$	$M_s = +1$	and	$M_j = +2$
Configuration 6	$M_l = +1$	$M_s = 0$	and	$M_j = +1$
Configuration 7	$M_l = +1$	$M_s = -1$	and	$M_j = 0$
Configuration 4	$M_l = 0$	$M_s = +1$	and	$M_j = +1$
Configuration 8	$M_l = 0$	$M_s = 0$	and	$M_j = 0$
Configuration 9	$M_l = 0$	$M_s = -1$	and	$M_j = -1$
Configuration 11	$M_l = -1$	$M_s = +1$	and	$M_j = 0$
Configuration 13	$M_l = -1$	$M_s = 0$	and	$M_j = -1$
Configuration 14	$M_l = -1$	$M_s = -1$	and	$M_j = -2$

For these configuration, we have

The value of spin multiplicity,  $2S + 1 = 2 \times 1 + 1 = 3$

The symbol for  $L = 1$  is P.

Hence, the term symbol for the above configurations is  $^3P$ . To insert the value of  $J$  in  $^3P$ , we proceed as follows.

- The maximum value of  $M_j$  is 2. This implies that  $J = 2$ . Associated with this, the values of  $M_j$  are +2, +1, 0, -1 and -2. Hence, 5 configurations out of the above listed 9 configurations belong to the term symbol  $^3P_2$ .

- Eliminating the above 5 configurations, we are left with 4 configurations with  $M_j = +1, 0, 0$  and  $-1$ .

The value of  $M_j$  equal to 1 implies that  $J = 1$ .

Associated with  $J = 1$ , the values of  $M_j$  are +1, 0 and -1. Hence, 3 configurations out of the remaining 4 configurations belong to the term symbol  $^3P_1$ .

- The only remaining configurations has  $M_j = 0$ . This implies that  $J = 0$ . Hence, this configuration belongs to the term symbol  $^3P_0$ .

**Comment on the Values of  $J$**  As mentioned earlier, the permitted values of  $J$  are  $L + S, L + S - 1, \dots, |L - S|$ . This gives  $J = 2, 1$  and 0 for  $L = 1$  and  $S = 1$  state.

- So far we have accounted for 14 configurations out of 15 configurations listed in Table 1.13.1. The only unaccounted configuration is 10, for which, we have

$M_l = 0$ . This implies that  $L = 0$

$M_s = 0$ . This implies that  $S = 0$

The value of spin multiplicity,  $2S + 1 = 2 \times 0 + 1 = 1$

The value of  $J (= L + S)$  is 0.

The term symbol for  $L = 0$  is S.

Hence, the configuration 10 belongs to the symbol  $^1S_0$ .

To sum up, the term symbols for the  $(1s)^2(2s)^2(2p)^2$  configurations are  $^1D_2, ^3P_2, ^3P_1, ^3P_0$  and  $^1S_0$ .

#### 1.14 HUND'S RULE

Hund's rules help in deciding the relative energies of various term symbols for a given electronic configuration. The rules are as follows.

- For states with the same value of  $L$ , the state with the largest value of  $S$  is the most stable. The stability decreases with decreasing value of  $S$ .
- For states with the same value of  $S$ , the state with the largest value of  $L$  is the most stable.
- If the states have the same value of  $L$  and  $S$ , then, for a subshell that is less than half filled, the state with the minimum value of  $J$  is the most stable. For a subshell that is more than half filled, the state with the maximum value of  $J$  is the most stable.

For the configuration  $nsn's$ , the term symbols are  $^3S_1$  and  $^1S_0$ . According to Hund's rule, the more stable state is the  $^3S_1$  state.

For the configuration  $(1s)^2(2s)^2(2p)^2$ , the term symbols are  $^1S_0, ^3P_0, ^3P_1, ^3P_2$  and  $^1D_2$ . According to Hund's rule, the most stable state is  $^3P_0$ .

Hund's rule is often stated as Hund's rule of maximum spin multiplicity. This follows from the fact that the spin multiplicity is given by  $2S + 1$ . Hence, larger the value of  $S$ , larger is the value of  $2S + 1$ .

#### Comment



According to Hund's rule, the configuration  $2p^2$  in which two electrons are assigned to different orbitals with the same spin has maximum spin multiplicity and hence is the most stable one. Qualitatively, Hund's rule can be understood on the basis of electron-electron interaction between the electrons. By occupying the different orbitals (i.e. quantum number  $m$  is different), two electrons are present in different regions and thus the electron-electron repulsive interaction is minimized. By having the same spin, the two electrons have the magnetic moment vectors in the same direction. Thus, the two tiny magnets have like poles near to each other and thereby repel each other to the maximum extent with the result that the two electrons remain far apart as much as possible. This further minimizes the electron-electron repulsive interaction. Had the two electrons been antiparallel (opposite spins), the north pole of one of the magnets would be near to south pole of the other and consequently would have attracted each other. This attraction would have decreased the distance between the two electrons and thus increased the electron-electron repulsive interaction.

### 1.15 THE AUFBAU PRINCIPLE AND THE ELECTRONIC CONFIGURATIONS OF ATOMS

Aufbau is a German word meaning building up. Thus, aufbau principle is the building up principle for writing the electronic configurations of various atoms.

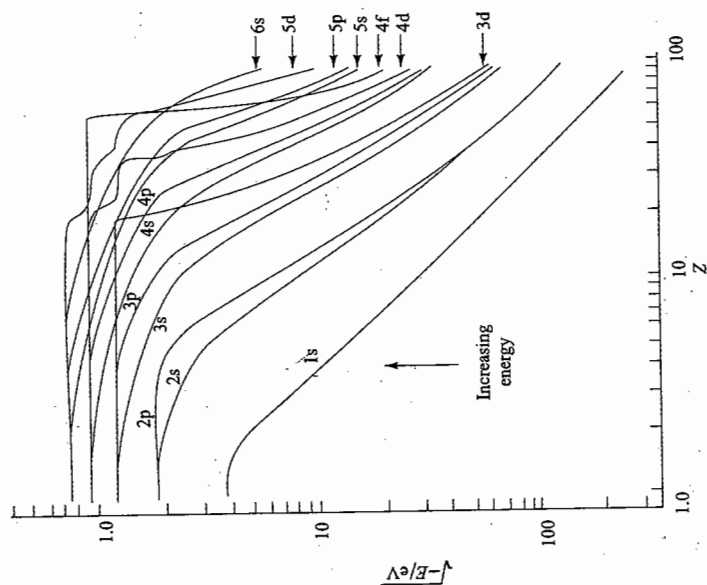


Fig. 1.15.1 Energy levels of atomic orbitals in the multi-electron atoms

According to this principle, the electrons are fed into various orbitals in the increasing order of energy consistent with Pauli exclusion principle and Hund's rule. This means that we should know the increasing order of energy of various orbitals in many-electron atoms. By employing the statistical common central potential-energy field it was possible to reproduce the SCF-orbital energies of multi-electron atoms. The resultant orbital energies are shown in Fig. 1.15.1. Following this figure, we can write the observed increasing order of energy of various orbitals as

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f \dots$$

This order can be easily generated by following the various arrows from top to bottom in the scheme shown in Fig. 1.15.2.

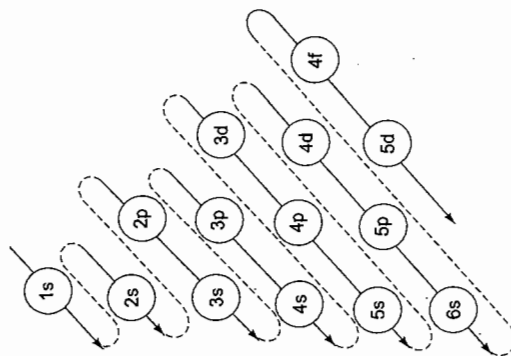


Fig. 1.15.2 Scheme to arrange the orbitals in the increasing order of energy

Following Fig. 1.15.1, we can write the electronic configuration of any atom in accordance with the aufbau principle, Pauli exclusion principle and Hund's rule. Table 1.15.1 illustrates the electronic configurations of first few elements of periodic table.

Table 1.15.1 Electronic Configurations of a Few Atoms

Atom	Electronic Configuration
H	$(1s)^1$
He	$(1s)^2$
Li	$(1s)^2(2s)^1$
Be	$(1s)^2(2s)^2$
B	$(1s)^2(2s)^2(2p)^1$
C	$(1s)^2(2s)^2(2p)^2$ or $(1s)^2(2s)^2(2p)^2$
N	$(1s)^2(2s)^2(2p)^3$ or $(1s)^2(2s)^2(2p)^3$
O	$(1s)^2(2s)^2(2p)^4$ or $(1s)^2(2s)^2(2p)^4$
F	$(1s)^2(2s)^2(2p)^5$ or $(1s)^2(2s)^2(2p)^5$
Ne	$(1s)^2(2s)^2(2p)^6$ or $(1s)^2(2s)^2(2p)^6$

## Electronic Configurations of Cr and Cu

Lastly, some comments about the electronic configurations of a few elements such as Cr, Cu, etc., may be made. The observed electronic configurations of Cr and Cu are  $(3d^5 4s^1)$  and  $(3d^{10} 4s^1)$  instead of  $(3d^4 4s^2)$  and  $(3d^9 4s^2)$ , respectively. These configurations have been explained on the basis of more stability of half-filled and completely filled orbitals as given below.

Since the electrons are indistinguishable, we can write down the wave function of an atom as a linear combination of electronic configurations differing only in the assignment of electrons (which are supposed to be numbered as 1, 2, 3, ...) to different atomic orbitals (e.g. Eqs 1.12.9 to 1.12.12). When the energy of such a wave function is evaluated by using the appropriate Schrödinger equation, two types of energies, viz., Coulomb and exchange energies, are involved. The Coulomb energy is a measure of the mean repulsion of two electrons occupying different orbitals. The exchange energy is the lowering of energy for a set of two electrons of parallel spins which arises as a result of indistinguishability of the electron coordinates. For a system containing more than two electrons of parallel spins, the lowering of energy due to exchange of electrons is given by

$$\Delta E = N \times K$$

where  $N$  is the total number of possible exchanges of coordinates between sets of two electrons of parallel spins and  $K$  is the average exchange energy per set of electrons of parallel spins. For a system containing  $n$  electrons of parallel spins,  $N$  is given by

$$N = \frac{n!}{2(n-2)!}$$

The exchange energies for the two possible configurations of Cr are as follows:

$$\begin{array}{ll} (3d^4 4s^2) & n = 5 \\ (3d^5 4s^1) & n = 6 \end{array} \quad \begin{array}{l} \Delta E = 10K \\ \Delta E = 15K \end{array}$$

that is, the exchange energy stabilization of  $(3d^5 4s^1)$  configuration is larger than that of  $(3d^4 4s^2)$  configuration. Besides this, since the two electrons with parallel spins remain farther apart than two electrons with opposed spins, the Coulombic repulsion energy is also smaller in case of two parallel spins. Thus the configurations  $(3d^5 4s^1)$ , which contains more number of parallel spins, is more stable than  $(3d^4 4s^2)$ . The stability of the  $(3d^{10} 4s^1)$  configuration for the copper atom may be explained in the same way.

Thus, it may be concluded that the unusual stability of electronic configurations involving half-filled and completely filled orbitals is due to the larger exchange energy and lesser Coulombic repulsion energy.

## REVISIONARY PROBLEMS

### Black-Body Radiation

- 1.1 (a) What is a black body? What types of radiations are emitted by such a body? Explain, why these radiations could not be rationalized on the basis of the classical theory of radiation.
- (b) Explain the following two laws as applicable to the black-body radiation:
  - (i) The Stefan-Boltzmann Law, and (ii) The Wien's displacement Law.
- (c) Outline, in brief, Wien's and Rayleigh-Jeans' contributions towards the explanation of energy spectra of a black body as a function of the wavelength. Show how Planck introduced the idea that the energy emitted from the black body is quantized and hence derive the Planck's expression:

$$E_\lambda = \frac{8\pi(hc/\lambda)}{\lambda^4 (\exp(hc/\lambda kT) - 1)}$$

- (d) Show that the Planck's radiation expression is reducible to the Rayleigh-Jeans equation and the Wien equation in the appropriate range of wavelength.
- (e) Starting with the Planck radiation law, derive the Wien's displacement law,  $\lambda_{\max} = (\text{constant})/T$ , where  $\lambda_{\max}$  is the wavelength at which  $E_\lambda$  has a maximum value for the given temperature.
- (f) Starting from the Planck radiation law, obtain the Stefan-Boltzmann law  $E = \sigma T^4$  where  $E$  is the total radiation energy from  $\lambda = 0$  to  $\lambda = \infty$ , that is

$$E = \int_0^\infty E_\lambda d\lambda = \sigma T^4$$

### Photoelectric Effect

### Bohr's Theory

- 1.2 Show how the Einstein extension of the idea of quantization to the radiation field could explain (i) the photoelectric effect, and (ii) the variation of heat capacity of monatomic solids with temperature.
- 1.3 (a) What is Bohr's contribution towards the structure of an atom? How did he account for the spectra of hydrogen atom? Derive the necessary formulae.
- (b) Comment upon the following:
  - (i) In spite of incorrect basis of Bohr's theory, the latter was successful in explaining the experimental spectra of hydrogen atom.
  - (ii) Explain which particular step in Bohr's theory was responsible for introducing the quantization of energy of the electron and its distance from the nucleus.
  - (iii) Discuss the merits and demerits of Bohr's theory.
  - (iv) What corrections are introduced if one considers the electron and the proton in the hydrogen atom to revolve about their centre of mass? On the basis of this, calculate the Rydberg constant for H and D atoms. What would be the predicted difference in wavelength of the first Balmer lines of H and D spectra?
- 1.4 Discuss the following with suitable illustrations.
  - (a) The wave-particle duality and the de Broglie's relation.
  - (b) The uncertainty principle.
  - (c) An experimental evidence for the wave nature of the electron.
  - (d) Larger the mass of a particle lesser the wave nature and hence explain why material particles of larger mass do not exhibit significant wave nature.
  - (e) Explain, why the motion of an electron cannot be described by the well-defined trajectories as is in the case of Bohr's theory.

### de Broglie Relation and Uncertainty Principle

### Schrödinger Equation from Standing Waves

(f) Show that a Bohr orbit for a hydrogen-like ion has a circumference that is an integral multiple of de Broglie wavelength of an electron of its momentum.

1.5 (a) Starting from the wave equation

$$\left(\frac{\partial^2 \psi}{\partial x^2}\right)_t = \frac{1}{u^2} \left(\frac{\partial^2 \psi}{\partial t^2}\right)_x$$

for the standing wave system, derive the Schrödinger equation

$$\left(\frac{\partial^2 \psi}{\partial x^2}\right) = -\frac{4\pi^2}{\lambda^2} \psi$$

(b) Employing the de Broglie relation and the relation  $p = \sqrt{2m(E - V)}$  for the electron in an atom, derive the Schrödinger equation

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

as applicable to the electron in an atom.

1.6 (a) Outline the essential postulates of quantum mechanics and using these postulates derive the Schrödinger equation as applicable to the electron in an atom.

(b) What is the physical significance of wave function? What is a normalized wave function?

(c) What do you understand by (i) an operator, (ii) eigenfunction, (iii) eigenvalue, (iv) linear operator, and (v) Hermitian operator?

1.7 (a) Set up the Schrödinger equation for a particle in a one-dimensional box. Show that the solution of Schrödinger equation leads to the quantization of translational motion and hence derive the energy expression

$$E = n^2 \left( \frac{h^2}{8ml^2} \right)$$

(b) What are the permitted values of quantum number  $n$ ? Explain, why a value of zero is not permitted.

(c) Show that for a free particle moving in an unbounded region of space, the translational energy is virtually unquantized. Show that the above statement is also true for a larger mass moving in a box of ordinary dimensions.

(d) Obtain the normalized wave function for the particle in a one-dimensional box. Plot the various wave functions and the corresponding probability density curves and thus show that the results for a very large value of  $n$  justify the Bohr's correspondence principle.

(e) Show how the model of particle in a box can be applied to calculate the energy spectra of polyenes.

(f) Set up the Schrödinger equation for the particle in a three-dimensional box. Solve it for the various allowed energies and the wave functions.

1.8 (a) What is a harmonic oscillator? For a particle oscillating around its mean position, show that

$$(i) \text{ The characteristic frequency } \nu_0 = (1/2\pi) \sqrt{k_t/m}$$

$$(ii) \text{ The potential energy } V = (1/2) k_t x^2$$

$$(iii) \text{ The total energy } E = (1/2) k_t A^2$$

where the various symbols have their usual meanings.

### Quantization of Vibrational Energy

### Quantization of Rotational Energy

(b) Set up the Schrödinger equation for a harmonic oscillator. Describe only the acceptable wave functions and the corresponding energies of the above Schrödinger equation. What is the zero-point energy? Show that the zero-point energy is consistent with the uncertainty principle.

(c) Show that the wave function for the lowest energy state of a harmonic oscillator is indeed a solution of Eq. (1.5.9).

(d) Show by plotting  $\psi$  and  $\psi^2$  that the time spent by an oscillator in its ground state is maximum at its mean position. How does this result tally with the classical results? How does the probability of finding the particles vary in the excited states? Do the quantum mechanical results for a very large value of the vibrational quantum number agree with those of classical results?

(e) Evaluate  $\langle x \rangle$  for a harmonic oscillator in its lowest and first excited energy states. Compare the results with those of Problems 1.5.3 and 1.5.4.

1.9 (a) What is a rigid rotator model? Utilizing the classical mechanics, show that

(i) The total energy of the rotator  $E = (1/2) I \omega^2$

(ii) The moment of inertia  $I = \mu r^2$

(iii) The angular momentum  $L = I \omega$

(b) Set up the Schrödinger equation for the system of a rigid rotator.

(c) The Schrödinger equation of Part (b) can be transformed into the spherical polar coordinates. Show that the transformed equation can be split into the following two equations:

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\varphi^2} = -m^2$$

$$\frac{1}{\Theta} \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + J(J+1) \sin^2 \theta = m^2$$

(d) Show that by a suitable transformation, the equation involving  $\Theta$  function can be written in the following more familiar form, known as the associated Legendre equation:

$$(1 - \xi^2) \frac{d^2 P}{d\xi^2} - 2\xi \frac{dP}{d\xi} + \left[ J(J+1) - \frac{m^2}{1 - \xi^2} \right] P = 0$$

where the function  $P$  is a function of the variable  $\xi$  ( $= \cos \theta$ ).

(e) Obtain the acceptable solutions of  $\Theta$  equation following the boundary condition of  $\Phi(\varphi + 2\pi) = \Phi(\varphi)$ .

(f) What quantum restriction on the value of  $m$  is introduced because of the above boundary condition?

(g) Obtain the expression for the normalized wave function  $\Phi$ .

(h) The acceptable solutions of the associated Legendre equation are the associated Legendre polynomials  $P_J^m$  where  $J$  is the degree and  $|m|$  is the order of the polynomial and are given by the relation

$$P_J^m = (1 - \xi^2)^{|m|/2} \frac{d^{|m|}}{d\xi^{|m|}} P_J$$

where  $P_J$  is the Legendre polynomial and is given by the relation

$$P_J = \frac{1}{2^J (J)!} \frac{d^J}{d\xi^J} (\xi^2 - 1)^J$$

What quantum restriction is placed on the value  $|m|$  relative to that of the constant  $J$ ?

(i) The normalized  $\Theta$ -function is given as

$$\Theta_{j, |m|} = \left[ \frac{(2j+1)(j-|m|)!}{2(j+|m|)!} \right]^{1/2} P_j^{(m)}$$

Using this expression, obtain the expressions for the  $\Theta$ -function for the following values of  $j$  and  $m$ .

$j$	0	1	1	2	2	2
$m$	0	0	$\pm 1$	0	$\pm 1$	$\pm 2$

- (j) What are the physical significances of the two quantum numbers  $j$  and  $m$ ?  
 (k) What do you understand by the term space quantization of angular momentum? Derive the relation

$$\sqrt{j(j+1)} \cos \theta = m_z$$

and hence show that the angle  $\theta$  cannot have all the values but only a few permitted values.

## Quantization of Electronic Energy

- (i) Derive the energy expression for a rigid rotator.  
 (m) The values of angular momentum and  $z$ -component of angular momentum have precise values. Is this a contradiction of uncertainty principle? Explain.  
 1.10 (a) Set up the Schrödinger equation for the hydrogen-like species. This equation can be split into the following two equations, one involving the motion of the atom as a whole and the other involving relative motion of the nucleus and electron.

$$-\frac{\hbar^2}{8\pi^2(m_e + m_n)} \left[ \frac{\partial^2}{\partial x_c^2} + \frac{\partial^2}{\partial y_c^2} + \frac{\partial^2}{\partial z_c^2} \right] \psi_M = E_{\text{total}} \psi_M$$

$$\left[ -\frac{\hbar^2}{8\pi^2\mu_e} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{(4\pi\epsilon_0)r} \right] \psi_e = E \psi_e$$

Starting from the equation which describes the motion of electron relative to the nucleus, show that it can be split into the following three equations.

$$(i) \frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{8\pi^2\mu r^2}{h^2} \left( E + \frac{Ze^2}{(4\pi\epsilon_0)r} \right) = l(l+1)$$

$$(ii) \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + l(l+1) \sin^2 \theta = m^2$$

$$(iii) \frac{1}{\Phi} \frac{d^2\Phi}{d\varphi^2} = -m^2$$

The  $\Theta$  and  $\Phi$  equations, i.e. Eqs (ii) and (iii) are identical to those of rigid rotator system and hence have the same  $\theta$  and  $\varphi$  solutions. The  $\Theta$  function depends on the two quantum numbers  $l$  and  $|m|$  and the  $\Phi$ -function only on the value of  $m$ .

Answer the following.

- (i) What are the permitted values of  $l$  and  $m$ ?  
 (ii) What are the physical significance of  $l$  and  $m$ ?  
 (iii) Derive the relation

$$\sqrt{l(l+1)} \cos \theta = m$$

where  $\theta$  is the angle between the angular momentum vector and the  $z$ -axis.

- (b) The radial equation can be written into the following more familiar form of associated Laguerre equation by suitable transformations.

$$\rho^2 \frac{d^2 L}{d\rho^2} + (j+1-\rho) \frac{dL}{d\rho} + (k-j)L = 0$$

where

$$j = 2l + 1$$

$$k = \lambda + l$$

$$\lambda = \frac{4\pi^2\mu Z e^2}{(4\pi\epsilon_0)\hbar^2 \alpha}$$

$$\alpha^2 = -\frac{8\pi^2\mu E}{h^2}$$

$$\rho = 2\alpha r$$

In deriving the above equation, the original function  $R(r)$  has been transformed into the function  $L(\rho)$  by the following transformations.

$$R(r) = s(\rho) = e^{-\rho/2} F(\rho) = \rho^l e^{-\rho/2} L_k(\rho)$$

The solution of the above associated Laguerre equation is given by the associated Laguerre polynomials  $L_k^j$  of degree  $(k-j)$  and order  $j$ , defined as

$$L \equiv L_k^j = \frac{d^j}{d\rho^j} L_k$$

where  $L_k$  is the Laguerre polynomial of degree  $k$  and is given by

$$L_k = e^\rho \frac{d^k}{d\rho^k} (\rho^k e^{-\rho})$$

The normalized form of the function  $R$  is given as

$$R = - \left\{ \left( \frac{2Z}{na_0} \right)^3 \frac{n(n-l-1)!}{2n!(n+l)!} \right\}^{1/2} \rho^{-l} e^{-\rho/2} L_{n+l}^{2l+1}$$

$$\text{where } \rho = (2\alpha r) = \left( \frac{4\pi^2\mu Z e^2}{(4\pi\epsilon_0)\hbar^2} \right) r = \left( \frac{2Z}{na_0} \right) r$$

Answer the following.

- (i) What are the quantum restrictions on the values of  $k$ ?  
 (ii) The variable  $\lambda$  can be written as  $n$ , where the latter can have only integral values.

- (iii) What quantum restrictions are imposed on the values of  $k$  relative to those of  $n$ . Hence show that

$$l \leq (n-1)$$

- (iv) Derive the relation

$$E = -\frac{1}{n^2} \left[ \frac{2\pi^2 \mu Z^2 e^4}{(4\pi\epsilon_0)^2 h^2} \right]$$

- (v) By employing the expression of the normalized  $R$ -wave function, obtain the expression for the  $R$ -function for each of the following values of  $n$  and  $l$ .

$n$	1	2	2	3	3	3
$l$	0	0	1	0	1	2

- (vi) Discuss the physical significances of the three quantum numbers  $n, l$  and  $m$ .

- 1.11 (a) Give schematic diagrams of wave functions, probability density distribution functions, electronic-cloud patterns, 90% probability contours and the radial distribution functions for 1s and 2s orbitals.

- (b) Give schematic diagrams of  $R$ -function, square of the  $R$ -function and the radial distribution function for the 2p orbitals.

- (c) Sketch the two-dimensional plots of  $\Theta_{1,0}$ ,  $\Theta_{1,1}^2$ ,  $(\Theta_{1,0}\Phi_0)$  and  $(\Theta_{1,0}\Phi_0)^2$  versus angle  $\theta$  in the  $yz$ -plane.

- (d) Discuss the directional characteristics of the function  $(\Theta_{1,0}\Phi_0)$ . Explain why the orbital containing this angular dependence is labelled as the  $2p_z$  orbital.

- (e) Construct the two real functions out of  $\Phi_{+1}$  and  $\Phi_{-1}$  functions and hence discuss the directional characteristics of angular dependence functions  $(\Theta\Phi_x)$  and  $(\Theta\Phi_y)$ . Explain, why the orbitals containing the above two angular dependences are called  $2p_x$  and  $2p_y$  orbitals, respectively.

- (f) Sketch the two-dimensional plots shown in Figs 1.8.11–1.8.15.

- (g) Discuss and directional characteristics of 3d orbitals giving due emphasis on the nodal plane and the labelling of the various orbitals.

- 1.12 (a) By employing the classical Ampere's law, derive the following relation for the electron

$$\mu_m = -gL$$

where  $\mu_m$  is the magnetic moment vector,  $L$  is the angular momentum vector, and  $g$  is the gyromagnetic ratio and is equal to  $e/2m$ . What is the significance of the negative sign in the above expression?

- (b) By employing the quantized expression of the angular momentum vector, derive the relation

$$\mu_m = -\mu_B \sqrt{l(l+1)}$$

where  $\mu_B$  is equal to  $eh/4\pi m_e$ , and is known as the Bohr magneton.

- (c) Derive the potential energy expression

$$V = +B\mu_B m$$

for the electron placed in a magnetic field  $B$  and hence discuss the splitting of the electronic energy of p orbitals in the presence of a magnetic field.

- (d) What is Zeeman effect? Discuss how a single transition  $2p \rightarrow 1s$  splits into three in the presence of a magnetic field.

- (e) What is anomalous Zeeman effect? How can this be explained on the basis of electron spin?

- (f) Explain the existence of double lines in the spectra of alkali metals.

- (g) Describe the Stern-Gerlach experiment. How does the experiment provide an explanation for the existence of electron spin?

- (h) What are the spin quantum numbers? Discuss their physical significance.
- 1.13 (a) Set up the Schrödinger equation for the many-electron atom and outline the factors which prevent a direct solution of this equation.

- (b) Taking an example of He atom, outline the perturbation method and the variation principle to improve upon the zeroth order wave functions.

- (c) Outline the self-consistent field (SCF) method of Hartree as applicable to the many-electron atoms. Explain, how in the SCF method the multi-electron problem is effectively reduced to one-electron problem. Describe the procedural part of the SCF method.

- (d) Explain, how in the SCF method the general framework of various orbitals of hydrogen-like species is still applicable for the many-electron atoms.

- (e) On what quantum numbers does the energy of an orbital in the multi-electron atoms depend?

- 1.14 (a) What do you understand by the indistinguishability of electron in an atom? What are the symmetric and antisymmetric total wave functions of the two-electron atom? Out of these, which one describes the experimental behaviour of the electron in an atom? Is it symmetric or antisymmetric total wave function? Explain, what do you understand by Pauli exclusion principle. Discuss the statement that no two electrons in an atom can have all the four quantum numbers identical.

- 1.15 What do you understand by atomic term symbol? Deduce the term symbols for the configurations (i)  $ns^2$ , (ii)  $nsn'l$ 's and (iii)  $(1s)^2(2s)^2(2p)^2$ .

- 1.16 What do you understand by Hund's rule and aufbau principle? In conjunction with Pauli's rule, explain how the various orbitals in a multi-electron atom are filled in.

- 1.17 Explain qualitatively why half-filled and completely filled orbitals are energetically more stable than other isoelectronic configurations.

## Many-Electron Atom

## Pauli's Principle

## Term Symbols

## Electronic Configuration

## TRY YOURSELF PROBLEMS

- 1.1 (a) Show that the function  $\psi = 8 \exp(5x)$  is an eigenfunction of the operator  $d^2/dx^2$ . What is the eigenvalue?  
 (b) Find the quantum-mechanical operator for  $p_x^3$   
 (c) Under what conditions is the function  $\exp(-aq^2)$  an eigenfunction of the operator

$$\frac{d^2}{dq^2} - kq^2$$

where  $k$  is constant?

(Hint: Eigenvalue should not contain terms involving  $q$ , so equate the terms involving  $q$  to zero.)

## 1.2 Laplacian operator

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

in spherical polar coordinates is given by

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

Show that the functions

- (i)  $1/r$ , (ii)  $\cos \theta$ , (iii)  $\sin \theta \sin \phi$ , and (iv)  $\sin^2 \theta \sin 2\phi$  are the eigenfunctions of Laplacian operator and find out their respective eigenvalues.

1.3 Show that  $3 \cos^2 \theta - 1$  is an eigenfunction of the operator

$$-\left(\frac{h}{2\pi}\right)^2 \left\{ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} \right\}$$

with the eigenvalue  $6(h/2\pi)^2$ .

## 1.4 Show that the functions:

- (i)  $\psi_1 = \exp(-ax^2)$  and (ii)  $\psi_2 = x \exp(-bx^2)$  are the eigenfunctions of the Schrödinger equation of a harmonic oscillator provided

$$a = b = \frac{\pi \sqrt{k/m}}{h}$$

Also show that the energy of the oscillator is equal to  $(h/4\pi) \sqrt{k/m}$  for the function  $\psi_1$  and  $(3h/4\pi) \sqrt{k/m}$  for function  $\psi_2$ .

(Hint: Evaluate  $H_{op}\psi$  and then put the terms other than constant equal to zero.

The constant term is equal to  $E$ .)

1.5 Show that the expectation value of momentum of a particle described by the wave function  $\exp(ikx)$  is  $h/2\pi k$ 

(Hint: Employ the relation  $\langle \psi^* | p_{op} | \psi \rangle = \langle \psi^* | \psi \rangle \langle \psi | p_{op} | \psi \rangle$ .)

1.6 (a) The  $z$ -component of angular momentum in classical mechanics is given by

$$L_z = x p_y - y p_x$$

Write down its operator in Cartesian coordinates and then convert it into spherical polar coordinates. Given:

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

(Hint: Use the expression

$$\frac{\partial}{\partial x} = \left( \frac{\partial r}{\partial x} \right) \frac{\partial}{\partial r} + \left( \frac{\partial \theta}{\partial x} \right) \frac{\partial}{\partial \theta} + \left( \frac{\partial \phi}{\partial x} \right) \frac{\partial}{\partial \phi} \text{ and similar expressions for } \partial/\partial y \text{ and } \partial/\partial z.)$$

$$\left[ \text{Ans. } \frac{h}{2\pi i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right), \frac{h}{2\pi i} \frac{\partial}{\partial \phi} \right]$$

(b) Since  $(L_z)_{op}$  depends only the angle  $\phi$ , its eigenfunctions will be a function of angle  $\phi$  only. Let it be

$$(L_z)_{op} \Phi = L_z \Phi$$

where  $L_z$  is the eigenvalue. By separating the variables, show that

$$\Phi = \exp(2\pi i L_z \phi / h)$$

(c) Since the function  $\Phi$  has to be a single-valued, it should satisfy the relation:

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

Show that this condition leads to the expression:

$$L_z = m(h/2\pi), \text{ where } m = 0, \pm 1, \pm 2, \dots$$

## 1.7 The particle in a box follows the relation

$$l = \frac{n\lambda}{2}, \quad n = 1, 2, 3, \dots$$

where  $l$  is the length of the box and  $\lambda$  is the wavelength of the particle. Invoking de Broglie relation  $p = h/\lambda$  in the above expression, show that the kinetic energy of the particle is given by

$$T = \frac{n^2 h^2}{8ml^2}$$

1.8 Using the variation function  $x(l-x)$ , calculate  $\langle x^2 \rangle$  for a particle in an one-dimensional box and compare it with the true ground state  $\langle x^2 \rangle$ .1.9 Show that  $n=0$  for a particle in one-dimensional box yields an infinitely large wavelength or uncertainty in position.

(Hint:  $n=0$  means  $E=0$ . Thus  $\Delta E = 0$  or  $\Delta p = 0$ . Hence,  $\Delta x$  is infinite according to uncertainty principle and  $\lambda$  is infinite according to de Broglie relation.)

1.10 The wave function for the lowest state of a harmonic oscillator has the form of a Gaussian function  $\exp(-ax^2)$ , where  $x$  is the displacement from equilibrium. Show that this function on substituting in the appropriate Schrödinger equation (1.5.9) gives

$$a = (\pi/h) \sqrt{mk} \text{ and } E = (1/2)(h/2\pi) \sqrt{k/m}$$

(Hint: After carrying out differentiation, put the terms involving  $x^2$  and constants separately equal to zero and  $E$ , respectively.)



- (b) Verify that the function  $\exp(-ax^2)$  where  $a = \sqrt{mk_e/2}(\hbar/2\pi)$  is an eigenfunction of the one-dimensional simple harmonic oscillation with an eigenvalue of  $(1/2)\hbar\nu$ .

- 1.11 For the ground state of a harmonic oscillator, calculate (a)  $\langle x \rangle$ ; (b)  $\langle x^2 \rangle$ ; and (c)  $\langle p_x \rangle$ .

- 1.12 With the variation function  $a x \exp(-cx^2)$  find the lowest energy of the harmonic oscillator. Explain why this energy is not equal to the correct energy  $(1/2)\hbar\nu_0$ . [Ans.  $(3/2)\hbar\nu_0$ ]

- 1.13 (a) Show that if  $l = 1$  and  $lml = 2$ , the associated Legendre polynomial vanishes, i.e.  $P_l^{lml} = 0$ .

- (b) The Legendre polynomial is given as

$$P_l = \frac{1}{2^l(l!)} \frac{d^l}{dx^l} (\xi^2 - 1)^l$$

Show that the highest power of  $\xi$  in this expression is  $\xi^l$ .

- (c) Show that the associated Legendre polynomial  $P_l^{lml}$  vanishes whenever  $lml > l$ .

- (d) Show that the associated Legendre polynomial  $P_l^{lml}$  reduces to the Legendre polynomial  $P_l$  when  $m = 0$ .

- 1.14 (a) Show that if  $n = 1$  and  $l = 1$ , the associated Laguerre polynomial vanishes, i.e.

$$L_{n+l}^{2l+1} = 0$$

- (b) Show that the highest power of  $\rho$  in the Laguerre polynomial is given by  $\rho^k$  and hence also show that the associated Laguerre polynomial vanishes whenever  $j > k$ .

- 1.15 (a) Sketch the allowed orientations with respect to an external magnetic field for the orbital angular momentum ( $L$ ) vector of a p electron in the hydrogen atom.

- (b) What is the length of the  $L$  vector?

- (c) Which of the orientations has the greatest energy?

- 1.16 With the variation function  $a \exp(-br)$  find the lowest energy of the hydrogen atom.

- 1.17 Calculate the velocity of 1s electron in an atom with nuclear charge  $Z$ . What value of  $Z$  would make the 1s electron travel at the velocity of light? Comment upon the implications of this result for the likelihood of producing an element with atomic number of about 140.

- 1.18 If  $\psi_1$  and  $\psi_2$  are wave functions for a degenerate state of energy  $E$ , prove that any linear combination  $c_1\psi_1 + c_2\psi_2$  is also a wave function.

- 1.19 Show that the probability of finding a  $2p_z$  electron in the  $xy$ -plane is zero.

- 1.20 Show that the radial distribution of 2s orbital of hydrogen atom exhibits two maxima at  $r$  equal to  $0.764a_0$  and  $5.236a_0$ , respectively.

(Hint: Put  $d(4\pi r^2 \psi_{20}^2)/dr = 0$  and simplify.)

- 1.21 Calculate the magnitude of the ground-state orbital angular momentum of the electron in a hydrogen atom according to (a) quantum mechanics, and (b) the Bohr's theory.

- 1.22 Given below are the values of three wave functions involving  $r$  of hydrogen atom for various values of  $r/a_0$ . Plot  $R$  versus  $r/a_0$ ,  $R^2$  versus  $r/a_0$  and  $4\pi r^2 R^2$  versus  $r/a_0$  and identify these wave functions. Compare your plots with those given in the text.

$r/a_0$	$R/10^{15} \text{ m}^{-1.5}$		
	(i)	(ii)	(iii)
0	5.20	1.84	—
0.125	4.59	1.62	—
0.25	4.05	1.42	0.12
0.50	3.15	1.07	0.21
1.00	1.91	0.56	0.32
1.5	1.16	0.22	0.38
2.0	0.70	0	0.39
2.5	0.43	—	—
3.0	0.26	-0.21	0.36
3.5	0.16	—	—
4.0	0.095	-0.25	0.29
5.0	—	-0.23	0.22
6.0	—	-0.18	0.16
7.0	—	-0.14	0.11

[Ans. (i)  $R_{1,0}$ , (ii)  $R_{2,0}$  and (iii)  $R_{2,1}$ ]

- 1.23 What is the degeneracy of the level of the hydrogen atom that has the energy:

(a)  $-R_H$ , (b)  $-R_H/9$ , and (c)  $-R_H/25$ ?

- 1.24 (a) According to the virial theorem, if the potential energy  $V$  is a homogeneous function of the coordinates of degree  $\rho$ , then

$$\langle T \rangle = \left( \frac{\rho}{2} \right) \langle V \rangle$$

The potential energy of a system made up of charged particles that interact solely by electrostatic forces is a homogeneous function of degree  $-1$ . Thus

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle$$

Show that the above theorem is satisfied by the electron in the ground state of the hydrogen atom for which the normalized wave function and energy operators in atomic units (see Annexure VII) are

$$\psi = \frac{1}{\sqrt{\pi}} \exp(-r)$$

$$T = -\left( \frac{1}{2r^2} \right) \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right)$$

$$V = -\frac{1}{r}$$

and the volume element is  $d\tau = 4\pi r^2 dr$ .

(b) If  $\langle E \rangle = \langle T \rangle + \langle V \rangle$ , what is the value of  $\langle E \rangle$  in atomic unit?

1.25 Calculate the expectation value of  $r$  for the hydrogen atom in the ground state.

Given:  $\int_0^\infty r^2 \exp(-2r/a_0) dr = 3!(2/a_0)^4$  [Ans.  $\langle r \rangle = (3/2)a_0$ ]

1.26 Which of the following transitions are allowed in the normal electronic spectrum of hydrogen atom?

(a)  $2s \rightarrow 1s$ , (b)  $2p \rightarrow 1s$ , (c)  $3d \rightarrow 2p$ , (d)  $5d \rightarrow 3s$ , (e)  $5p \rightarrow 3s$ .

1.27 The characteristic emission from potassium when heated is purple and lies at 770 nm. On close inspection the line is seen to be composed of two closely spaced components, one at 766.70 nm and the other at 770.11 nm. Account for this observation.

1.28 (a) Show that the hydrogen wave function for  $l = 1$  have maxima along the directions of the Cartesian axes.

(b) Show that the radial distribution function of  $2p$  orbital of hydrogen atom exhibits one maximum at  $r = 4a_0$ .

1.29 Show that the configurations consisting of a completely filled or half-filled set of  $d$  orbitals is spherically symmetrical. Which of the following species has spherical symmetry? Na,  $\text{Na}^+$ , Al, Zn, N, F,  $\text{O}^{2-}$ , Cr

1.30 (a) The  $3s$  orbital has two radial nodes. Calculate the value of  $r$  in terms of  $a_0$  at which these two nodes are observed.

(b) The  $3p$  orbital has one radial node. Calculate the value of  $r$  in terms of  $a_0$  at which this node is observed.

(c) How many radial and angular nodes are present in the  $3d$  orbital?

1.31 Find the value of  $r$  for which the radial distribution function for the  $2s$  state of the hydrogen atom has a maximum or a minimum.

1.32 Which of the following wave functions satisfy the principle of indistinguishability of electrons and the Pauli principle?

(a)  $1s(1)2s(2)\alpha(1)\beta(2)$ .

(b)  $(1/2) [1s(1)2s(2) - 2s(1)1s(2)] [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ .

(c)  $(1/\sqrt{2}) [1s(1)2s(2)\alpha(1)\beta(2) - 2s(1)1s(2)\beta(1)\alpha(2)]$ .

(d)  $(1/\sqrt{2}) [1s(1)2s(2) + 2s(1)1s(2)] \alpha(1)\alpha(2)$ .

1.33 Give the magnitude of the angular momentum of an electron that occupies the following orbitals:

(a)  $1s$ , (b)  $3s$ , (c)  $3d$ , (d)  $2p$  and (e)  $3p$ .

Give the number of radial and angular nodes in each case.

1.34 The antisymmetric wave functions can be written in the form of determinant, known as *Slater determinant*. For example, the wave function as given by Eq. (1.12.10) is

$$\frac{1}{\sqrt{2}} [\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)] [\alpha(1)\alpha(2)]$$

i.e.  $\frac{1}{\sqrt{2}} [\phi_1(1)\alpha(1)\phi_2(2)\alpha(2) - \phi_1(2)\alpha(2)\phi_2(1)\alpha(1)]$

The above expression can be generated from the determinant

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\alpha(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\alpha(2) \end{vmatrix}$$

If in the above determinant  $\phi_1 = \phi_2$ , then the two rows of the determinant are identical and hence its value is zero. This is, in fact, the Pauli exclusion principle according to which the same orbital cannot hold two electrons of the same spin.

(a) Show that the wave function of Eq. (1.12.9) can be written as the sum of two determinants

$$\begin{vmatrix} \phi_1(1)\alpha(1) & \phi_2(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_2(2)\beta(2) \end{vmatrix} - \begin{vmatrix} \phi_1(1)\beta(1) & \phi_2(1)\alpha(1) \\ \phi_1(2)\beta(2) & \phi_2(2)\alpha(2) \end{vmatrix}$$

(b) Is the sum of the above two determinants zero for  $\phi_1 = \phi_2$ ? Does the conclusion agree with the Pauli exclusion principle?

1.35 The zero-point energies are a manifestation of the uncertainty principle. Discuss the above statement in the light of the following facts.

'The electron in a hydrogen atom and a harmonic oscillator have nonvanishing zero-point energy whereas the zero-point energy of a rotator is zero.'

1.36 Derive the atomic term symbols for the following configurations.

(a)  $1s2p$ , (b)  $1s2s$ , (c)  $(1s)^2(2s)^22p3p$ , and (d)  $(1s)^2(2s)^22p3d$

[Ans. (a)  $^1P$ ,  $^3P$ ; (b)  $^3S$ ,  $^1S$ ; (c)  $^3S$ ,  $^3P$ ,  $^1S$ ,  $^1P$ ; (d)  $^1P$ ,  $^3P$ ,  $^1D$ ,  $^3D$ ,  $^1F$ ,  $^3F$ ]

1.37 Show that  $\psi_{1s(H)}$  and  $\psi_{2s(H)}$  are orthogonal to each other.

1.38 Show that the most probable distance of an electron in the  $2p$  orbital of hydrogen atom is  $4a_0$ .

[Hint: Find  $r$  using the expression  $d(r^2R^2)/dr = 0$ .]

1.39 Compute  $\langle r \rangle$  for the  $2s$ ,  $2p$ , and  $3s$  states of a hydrogen atom and compare the results with the general expression  $\langle r \rangle = \frac{a_0}{2} [3n^2 - l(l+1)]$ .

1.40 Evaluate the commutators of each of the following.

$(x, d/dx)$ ,  $(y, d/dx)$  and  $(d/dx, d^2/dx^2)$  [Ans.  $-1, 0, 0$ ]

1.41 Show that the operators  $3x^2$  and  $d/dx$  do not commute with each other.

1.42 Show that the probability of finding  $1s$  electron in a hydrogen atom within one Bohr radius is 0.323.

1.43 Show that for  $1s$  electron in a hydrogen atom  $\langle r \rangle = (3/2)r_{\text{mp}}$ .

1.44 Determine the minimum energy of a particle in a one-dimensional box ( $V = 0$  for  $0 < x < l$  and  $V = \infty$  elsewhere) by using the wave function

$$\psi = C_1 x(l-x) + C_2 x^2(l-x)^2$$

[Hint: See Annexure XII.]



## NUMERICAL PROBLEMS

## Black-Body Radiation

- 1.1 Given below are the wavelengths of emission maximum from a small pinhole of a container at different temperatures.

$T/K$	1 273	1 773	2 273	2 723	3 273	3 773
$\lambda_{\max}/\text{nm}$	2 180	1 600	1 240	1 035	878	763

Deduce graphically the value of Planck's constant.

(Hint: Plot  $\lambda_{\max}$  versus  $1/T$ , slope =  $hc/5k$ , Eq. 1.1.19.)

- 1.2 The following values for the retarding potentials at which the photoelectric current from a sodium surface was reduced to zero were obtained.

$\lambda/\text{nm}$	312.5	365.0	404.7	433.9	546.1
$V_r/V$	2.128	1.595	1.215	1.025	0.467

Calculate (a) the threshold frequency, and (b) Planck's constant.

(Hint: Plot  $V_r$  versus  $1/\lambda$ , slope =  $hc/e$ , Eq. 1.1.23.)

## Particle in a Box

- 1.3 Benzene may be regarded as a two-dimensional box of side about 0.35 nm and containing six electrons. What wavelength of light should be required to promote an electron from the ground to the first excited state?

[Ans. 135 nm]

- 1.4 Naphthalene may be considered to be a rectangle of length and breadth equal to 0.7 nm and 0.4 nm, respectively. Derive the appropriate energy expression for a particle in a rectangular box and calculate the expected wavenumber of radiation required to give the first excited state.

- 1.5 The diameter of a typical small nucleus is about  $10^{-13}$  cm. Suppose that a proton is held in a one-dimensional potential well with infinite walls and a width of  $10^{-13}$  cm. Calculate the first three energy levels in eV. Suppose an electron is placed in this box, what would be the lowest energy level? From this result, conclude whether an electron can exist within the nucleus or not.

- 1.6 A particle of charge equal to that of an electron and mass 208 times the mass of the electron moves in a circular orbit around a nucleus of charge  $+3e$ . Assuming that the Bohr model of the atom is applicable to this system, (a) derive the expression for the radius of the  $n$ th Bohr orbit, (b) determine the value of  $n$  for which the radius of the orbit is approximately the same as that of the first Bohr orbit for the hydrogen atom, and (c) determine the wavelength of the radiation emitted when the revolving particle jumps from the third orbit to the first.

[Ans. (a)  $r = n^2(8.51 \times 10^{-14} \text{ m})$ , (b)  $n = 25$ , (c)  $\lambda = 55.2 \text{ pm}$ ]

- 1.7 The hypothetical element positronium consists of an electron moving in space around a nucleus consisting of a positron (a subatomic particle similar to the electron except possessing a positive charge). Using the Bohr's theory calculate the radius of the first orbit of the electron.

[Ans. 106 pm, use  $\mu$  instead of  $m_e$ ]

- 1.8 Calculate the magnetic moment of a particle with charge  $2.0 \times 10^{-16} \text{ C}$  moving in a circle of radius 2.5 nm with speed  $2.0 \times 10^5 \text{ m s}^{-1}$ .

[Ans.  $5.0 \times 10^{-20} \text{ J T}^{-1}$ ]

## ANNEXURE I

## Derivation of de Broglie Relation for a Photon

According to theory of relativity, the mass of a particle varies with its velocity according to the expression

$$m = \frac{m_0}{\{1 - (v^2/c^2)\}^{1/2}} \quad (\text{A1.1})$$

where  $m_0$ , the mass as  $v \rightarrow 0$ , is called the rest mass of the particle. The expression of its momentum will be given by

$$p = \frac{m_0 v}{\{1 - (v^2/c^2)\}^{1/2}} \quad (\text{A1.2})$$

For a photon, though  $m_0 = 0$ , its momentum is not necessarily zero because for  $v = c$ , Eq. (A1.2) gives

$$p = \frac{0}{0}$$

an indeterminate quantity. To determine the value of  $p$  for a photon, we proceed as follows.

The kinetic energy of a particle may be defined as the work that is required to accelerate a particle from rest to its final velocity  $v$ , i.e.

$$T = \int_{v=0}^{v=v} dw = \int_{v=0}^{v=v} F dx$$

According to Newton's second law, the above expression becomes

$$T = \int_{v=0}^{v=v} (ma) dx = \int_{v=0}^{v=v} m \frac{dv}{dt} dx = \int_{v=0}^{v=v} d(mv) \frac{dx}{dt} = \int_{v=0}^{v=v} v d(mv) \quad (\text{A1.3})$$

For a nonrelativistic (or classical) mechanics,  $m$  is independent of  $v$ , hence we get the classical expression of kinetic energy, i.e.

$$T = m \int_0^v v dv = \frac{1}{2} m v^2$$

For a relativistic mechanics,  $m$  varies with velocity  $v$  according to Eq. (A1.1). Hence

$$\begin{aligned} T &= \int_0^v v d \left( \frac{m_0 v}{\{1 - (v^2/c^2)\}^{1/2}} \right) = \int_0^v \frac{m_0 v}{\{1 - (v^2/c^2)\}^{3/2}} dv \\ &= m_0 c^2 \left[ \frac{1}{\{1 - (v^2/c^2)\}^{1/2}} - 1 \right] \end{aligned} \quad (\text{A1.4})$$

[Note that Eq. (AI.4) gives the classical result of  $T = (1/2) mv^2$  when  $(v/c) \rightarrow 0$ . To prove this, we write  $\{1 - (v^2/c^2)\}^{-1/2}$  as  $1 + (1/2)(v^2/c^2)$  and substitute in Eq. (AI.4) which gives  $T = (1/2) mv^2$ ]

Invoking Eq. (AI.1) in Eq. (AI.4), we get

$$T = mc^2 - m_0c^2 \quad (\text{AI.5})$$

The terms  $mc^2$  and  $m_0c^2$  in Eq. (AI.5) represent the *total energy* and *rest energy* of the particle, respectively. Hence, we write Eq. (AI.5) as

$$E = T + m_0c^2 \quad (\text{AI.6})$$

From Eq. (AI.2), it can be shown that

$$\frac{v^2}{c^2} = \frac{p^2}{m_0^2c^2 + p^2}$$

Substituting the above expression in Eq. (AI.4), we get

$$T = m_0c^2 \left[ \frac{1}{\{1 - p^2/(m_0^2c^2 + p^2)\}^{1/2}} - 1 \right]$$

$$\text{or } T + m_0c^2 = \frac{m_0c^2(m_0^2c^2 + p^2)^{1/2}}{(m_0^2c^2)^{1/2}} = c(m_0^2c^2 + p^2)^{1/2}$$

Squaring on both sides, we get

$$(T + m_0c^2)^2 = c^2(m_0^2c^2 + p^2)$$

which on substituting in Eq. (AI.6) gives

$$E^2 = (pc)^2 + (m_0c^2)^2 \quad (\text{AI.7})$$

Using Planck's equation  $E = hc/\lambda$  in Eq. (AI.7), we get

$$\left(\frac{hc}{\lambda}\right)^2 = (pc)^2 + (m_0c^2)^2 \quad (\text{AI.8})$$

For a photon,  $m_0 = 0$ , hence

$$\left(\frac{hc}{\lambda}\right)^2 = (pc)^2$$

$$\text{or } p = \frac{h}{\lambda} \quad (\text{AI.9})$$

Equation (AI.9) is the required expression connecting particle nature (i.e.  $p$ ) with the wave nature (i.e.  $\lambda$ ) of a photon. According to de Broglie, Eq. (AI.9) is, as well, applicable to all material particles.

## ANNEXURE II Solutions of Schrödinger Equation for a Harmonic Oscillator

### THE POWER SERIES METHOD

#### Expression of Schrödinger Equation

The Schrödinger equation of a particle executing simple harmonic motion is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} \left(E - \frac{1}{2}k_f x^2\right) \psi = 0 \quad (\text{AII.1})$$

Let we represent

$$\lambda = \frac{8\pi^2m}{h^2} E \quad (\text{AII.2})$$

$$\text{and } \alpha^2 = \frac{8\pi^2m}{h^2} \left(\frac{1}{2}k_f\right) \quad (\text{AII.3})$$

With these, Eq. (AII.1) becomes

$$\frac{d^2\psi}{dx^2} + (\lambda - \alpha^2 x^2) \psi = 0$$

This equation is simplified by using the substitution

$$y = \sqrt{\alpha} x \quad (\text{AII.4})$$

which gives

$$\alpha \frac{d^2\psi}{dy^2} + (\lambda - \alpha y^2) \psi = 0, \quad \text{i.e.} \quad \frac{d^2\psi}{dy^2} + \left(\frac{\lambda}{\alpha} - y^2\right) \psi = 0 \quad (\text{AII.5})$$

For asymptotic solution of Eq. (AII.5), we set  $y^2 \gg \lambda/\alpha$ , such that Eq. (AII.5) is reduced to

$$\frac{d^2\psi}{dy^2} - y^2 \psi = 0$$

The solution of this equation is

$$\psi = e^{-y^2/2} \quad (\text{AII.6})$$

(Note: The solution  $e^{y^2/2}$  is rejected as  $\psi \rightarrow \infty$  as  $y \rightarrow \infty$ .)

With the asymptotic solution  $\psi = e^{-y^2/2}$ , the solution of Eq. (AII.5) may be expressed as

$$\psi = H e^{-y^2/2} \quad (\text{AII.7})$$

where  $H$  is a function of  $y$  and is yet to be determined.

**Hermite's Equation**

From Eq. (AII.7), we have

$$\begin{aligned}\frac{d\psi}{dy} &= \left(\frac{dH}{dy}\right) e^{-y^2/2} + H \left(\frac{-2y}{2}\right) e^{-y^2/2} = \left(\frac{dH}{dy} - yH\right) e^{-y^2/2} \\ \frac{d^2\psi}{dy^2} &= \left(\frac{d^2H}{dy^2} - H - y\frac{dH}{dy}\right) e^{-y^2/2} + \left(\frac{dH}{dy} - yH\right) \left(\frac{-2y}{2}\right) e^{-y^2/2} \\ &= \left[\frac{d^2H}{dy^2} - 2y\frac{dH}{dy} + (y^2 - 1)H\right] e^{-y^2/2}\end{aligned}$$

With these, Eq. (AII.5) becomes

$$\left[\frac{d^2H}{dy^2} - 2y\frac{dH}{dy} + (y^2 - 1)H\right] e^{-y^2/2} + \left(\frac{\lambda}{\alpha} - y^2\right) H e^{-y^2/2} = 0$$

$$\text{or } \left[\frac{d^2H}{dy^2} - 2y\frac{dH}{dy} + \left(\frac{\lambda}{\alpha} - 1\right)H\right] e^{-y^2/2} = 0$$

$$\text{or } \frac{d^2H}{dy^2} - 2y\frac{dH}{dy} + \left(\frac{\lambda}{\alpha} - 1\right)H = 0 \quad (\text{AII.8})$$

Equation (AII.8) is known as Hermite's equation.

**Solution of Eq. (AII.8) by the Power Series Method**

In the series method, the function  $H$  is expressed as a power series in  $y$ .

$$H = a_0 + a_1 y + a_2 y^2 + a_3 y^3 + a_4 y^4 + \dots \quad (\text{AII.9})$$

From this series, we get

$$\frac{dH}{dy} = a_1 + 2a_2 y + 3a_3 y^2 + 4a_4 y^3 + \dots \quad (\text{AII.10})$$

$$\text{and } \frac{d^2H}{dy^2} = (1 \times 2)a_2 + (2 \times 3)a_3 y + (3 \times 4)a_4 y^2 + \dots \quad (\text{AII.11})$$

Substituting Eqs (AII.9) to (AII.11) in Eq. (AII.8), we get

$$\begin{aligned}[(1 \times 2)a_2 + (2 \times 3)a_3 y + (3 \times 4)a_4 y^2 + \dots] - 2y[a_1 + 2a_2 y + 3a_3 y^2 + 4a_4 y^3 + \dots] + \left(\frac{\lambda}{\alpha} - 1\right)[a_0 + a_1 y + a_2 y^2 + a_3 y^3 + \dots] = 0\end{aligned}$$

that is

$$\begin{aligned}&\left[(1 \times 2)a_2 + \left(\frac{\lambda}{\alpha} - 1\right)a_0\right] + \left[(2 \times 3)a_3 + \left(\frac{\lambda}{\alpha} - 1 - 2\right)a_1\right] y \\&+ \left[(3 \times 4)a_4 + \left(\frac{\lambda}{\alpha} - 1 - 2 \times 2\right)a_2\right] y^2 \\&+ \left[(4 \times 5)a_5 + \left(\frac{\lambda}{\alpha} - 1 - 2 \times 3\right)a_3\right] y^3 + \dots = 0\end{aligned}$$

**Restriction of Power Series to Finite Number of Terms**

The power series as given by Eq. (AII.9) gives  $H \rightarrow \infty$  as the value of  $y \rightarrow \infty$ . To avoid this, we choose values of  $\lambda/\alpha$  in Eq. (AII.12) such that the value of  $a_v$  becomes zero after a certain number of terms so that we have polynomial solutions instead of power series. This is achieved by setting

$$\frac{\lambda}{\alpha} - 1 - 2v = 0; \quad v = 0, 1, 2, \dots \quad (\text{AII.13})$$

in Eq. (AII.12)

From Eq. (AII.12), we can write the expressions of coefficients  $a_v$

**Case 1 When  $v$  has even values**

$$\text{For } v = 0 \quad a_2 = -\frac{1}{1 \times 2} \left(\frac{\lambda}{\alpha} - 1\right) a_0$$

$$\text{For } v = 2 \quad a_4 = -\frac{1}{3 \times 4} \left(\frac{\lambda}{\alpha} - 1 - 2 \times 2\right) a_2$$

$$\begin{aligned}&= \left[-\frac{1}{3 \times 4} \left(\frac{\lambda}{\alpha} - 1 - 2 \times 2\right)\right] \left[-\frac{1}{1 \times 2} \left(\frac{\lambda}{\alpha} - 1\right) a_0\right] \\&= \frac{1}{4!} \left(\frac{\lambda}{\alpha} - 1\right) \left(\frac{\lambda}{\alpha} - 1 - 2 \times 2\right) a_0\end{aligned}$$

For the above expression to be true for all values of  $y$ , each of the coefficients must be separately equal to zero. This gives

$$(1 \times 2)a_2 + \left(\frac{\lambda}{\alpha} - 1\right)a_0 = 0$$

$$(2 \times 3)a_3 + \left(\frac{\lambda}{\alpha} - 1 - 2\right)a_1 = 0$$

$$(3 \times 4)a_4 + \left(\frac{\lambda}{\alpha} - 1 - 2 \times 2\right)a_2 = 0$$

$$(4 \times 5)a_5 + \left(\frac{\lambda}{\alpha} - 1 - 2 \times 3\right)a_3 = 0$$

and so on.

The above equalities may be represented by the general expression

$$(v+1)(v+2)a_{v+2} + \left(\frac{\lambda}{\alpha} - 1 - 2v\right)a_v = 0; \quad v = 0, 1, 2, \dots \quad (\text{AII.12})$$

Equation (AII.12) is known as recursion formula. It permits the computation of the coefficient  $a_{v+2}$  in terms of the coefficient  $a_v$ , if we set  $a_1 = 0$  arbitrarily, we can compute  $a_2, a_4, a_6$ , etc., in terms of  $a_0$ . Similarly, if we set  $a_0 = 0$  arbitrarily, we can compute  $a_3, a_5, a_7$ , etc., in terms of  $a_1$ .

The power series as given by Eq. (AII.9) gives  $H \rightarrow \infty$  as the value of  $y \rightarrow \infty$ . To avoid this, we choose values of  $\lambda/\alpha$  in Eq. (AII.12) such that the value of  $a_v$  becomes zero after a certain number of terms so that we have polynomial solutions instead of power series. This is achieved by setting

For  $v = 4$   $a_6 = -\frac{1}{5 \times 6} \left( \frac{\lambda}{\alpha} - 1 - 2 \times 4 \right) a_4$

$$= \left[ -\frac{1}{5 \times 6} \left( \frac{\lambda}{\alpha} - 1 - 2 \times 4 \right) \right] \left[ \frac{1}{4!} \left( \frac{\lambda}{\alpha} - 1 \right) \left( \frac{\lambda}{\alpha} - 1 - 2 \times 2 \right) a_0 \right]$$

$$= -\frac{1}{6!} \left( \frac{\lambda}{\alpha} - 1 \right) \left( \frac{\lambda}{\alpha} - 1 - 2 \times 2 \right) \left( \frac{\lambda}{\alpha} - 1 - 2 \times 4 \right) a_0$$

and so on.

Substituting  $\frac{\lambda}{\alpha} - 1 = 2v$  (from Eq. AII.13) in the above expressions, we get

$$a_2 = -\frac{1}{1 \times 2} (2v) a_0 = -\frac{2v}{2!} a_0$$

$$a_4 = -\frac{1}{4!} (2v) (2v - 4) a_0 = -\frac{2^2 v(v-2)}{4!} a_0$$

$$a_6 = -\frac{1}{6!} (2v) (2v - 4) (2v - 8) a_0 = -\frac{2^3 v(v-2)(v-4)}{6!} a_0$$

and so on.

With these, the explicit expression of  $H_v$  for  $v$  even is given by

$$H_v = a_0 \left[ 1 - \frac{2v}{2!} y^2 + \frac{2^2 v(v-2)}{4!} y^4 - \frac{2^3 v(v-2)(v-4)}{6!} y^6 + \dots \right]$$

(AII.14)

It is customary to choose  $a_0$  such that the coefficient of the highest power of  $y$ , that is  $y^v$ , is  $2^v$ . With this, the above expression of  $H_v$  may be written as

$$H_v = (-1)^{v/2} \frac{v!}{(v/2)!} \left[ 1 - \frac{2v}{2!} y^2 + \frac{2^2 v(v-2)}{4!} y^4 - \frac{2^3 v(v-2)(v-4)}{6!} y^6 + \dots \right]$$

(AII.15)

## Case 2 When $v$ has odd values

For  $v = 1$   $a_3 = -\frac{1}{2 \times 3} \left( \frac{\lambda}{\alpha} - 1 - 2 \right) a_1$

For  $v = 3$   $a_5 = -\frac{1}{4 \times 5} \left( \frac{\lambda}{\alpha} - 1 - 2 \times 3 \right) a_3$

$$= \left[ -\frac{1}{4 \times 5} \left( \frac{\lambda}{\alpha} - 1 - 2 \times 3 \right) \right] \left[ -\frac{1}{2 \times 3} \left( \frac{\lambda}{\alpha} - 1 - 2 \right) a_0 \right]$$

$$= \frac{1}{5!} \left( \frac{\lambda}{\alpha} - 1 - 2 \right) \left( \frac{\lambda}{\alpha} - 1 - 2 \times 3 \right) a_1$$

For  $v = 5$   $a_7 = -\frac{1}{6 \times 7} \left( \frac{\lambda}{\alpha} - 1 - 2 \times 5 \right) a_5$

$$= \left[ -\frac{1}{6 \times 7} \left( \frac{\lambda}{\alpha} - 1 - 2 \times 5 \right) \right] \left[ \frac{1}{5!} \left( \frac{\lambda}{\alpha} - 1 - 2 \right) \left( \frac{\lambda}{\alpha} - 1 - 2 \times 3 \right) a_1 \right]$$

$$= -\frac{1}{7!} \left( \frac{\lambda}{\alpha} - 1 - 2 \right) \left( \frac{\lambda}{\alpha} - 1 - 2 \times 3 \right) \left( \frac{\lambda}{\alpha} - 1 - 2 \times 5 \right) a_1$$

and so on.

Substituting  $\frac{\lambda}{\alpha} - 1 = 2v$  (from Eq. AII.13) in the above expressions, we get

$$a_3 = -\frac{2(v-1)}{3!} a_1$$

$$a_5 = -\frac{2^2(v-1)(v-3)}{5!} a_1$$

$$a_7 = -\frac{2^3(v-1)(v-3)(v-5)}{7!} a_1$$

and so on.

Hence, the explicit expression of  $H_v$  for  $v$  odd is given by

$$H_v = a_1 \left[ y - \frac{2(v-1)}{3!} y^3 + \frac{2^2(v-1)(v-3)}{5!} y^5 - \frac{2^3(v-1)(v-3)(v-5)}{7!} y^7 + \dots \right] \quad (\text{AII.16})$$

It is customary to choose  $a_1$  such that the coefficient of the highest power of  $y$ , that is  $y^v$ , is  $2^v$ . With this, the above expression of  $H_v$  may be written as

$$H_v = (-1)^{(v-1)/2} \frac{2(v!)}{[(v-1)/2]!} \left[ y - \frac{2(v-1)}{3!} y^3 + \frac{2^2(v-1)(v-3)}{5!} y^5 - \frac{2^3(v-1)(v-3)(v-5)}{7!} y^7 + \dots \right] \quad (\text{AII.17})$$

The normalization constant of the function  $\psi$  (Eq. AII.7) may be computed by evaluating the integral

$$\int_{-\infty}^{+\infty} (NH_v e^{-y^2/2})^2 dx = 1$$

Since  $y = \sqrt{\alpha}x$ , we get

$$\frac{N^2}{\sqrt{\alpha}} \int_{-\infty}^{+\infty} H_v^2 e^{-y^2} dy = 1$$

The value of integral is equal to  $2^v v! \sqrt{\pi}$ . Hence

$$\frac{N^2}{\sqrt{\alpha}} (2^v v! \sqrt{\pi}) = 1$$

$$\text{or } N = \left( \frac{\sqrt{\alpha}}{2^v v! \sqrt{\pi}} \right)^{1/2} \quad (\text{AII.18})$$

From Eq. (AII.13), we have

$$\frac{\lambda}{\alpha} - 1 - 2v = 0; \quad v = 0, 1, 2, \dots$$

Substituting the expressions of  $\lambda$  and  $\alpha$  from Eqs (AII.2) and (AII.3), we get

$$\frac{8\pi^2 m E / h^2}{2\pi \sqrt{mk_f / h}} - 1 - 2v = 0; \quad v = 0, 1, 2, \dots$$

Rearranging this expression, we get

$$E = \frac{h}{2\pi} \sqrt{\frac{k_f}{m}} \left( v + \frac{1}{2} \right) = h\nu_0 \left( v + \frac{1}{2} \right); \quad v = 0, 1, 2, \dots \quad (\text{AII.19})$$

where  $\nu_0$  is the classical frequency of the oscillator.

The expressions of Hermite polynomials can be conveniently generated by using the relation

$$H_v = (-1)^v e^{y^2} \frac{d^v}{dy^v} (e^{-y^2}) \quad (\text{AII.20})$$

For example, we have

$$\begin{aligned} v=0 \quad H_0 &= (-1)^0 e^{y^2} \frac{d^0}{dy^0} (e^{-y^2}) = e^{y^2} e^{-y^2} = 1 \\ v=1 \quad H_1 &= (-1)^1 e^{y^2} \frac{d}{dy} (e^{-y^2}) = (-1) e^{y^2} (-2y e^{-y^2}) = 2y \\ v=2 \quad H_2 &= (-1)^2 e^{y^2} \frac{d^2}{dy^2} (e^{-y^2}) = (-1)^2 e^{y^2} \frac{d}{dy} (-2y e^{-y^2}) \\ &= (-1)^2 e^{y^2} (-2e^{-y^2} + 4y^2 e^{-y^2}) = 4y^2 - 2 \end{aligned}$$

and so on,

By definition

$$H_v = (-1)^v e^{y^2} \frac{d^v}{dy^v} (e^{-y^2}) \quad (\text{Eq. AII.20})$$

$$\begin{aligned} \text{Hence } \frac{dH_v}{dy} &= (-1)^v (2ye^{y^2}) \frac{d^v}{dy^v} (e^{-y^2}) + (-1)^v e^{y^2} \frac{d^{v+1}}{dy^{v+1}} (e^{-y^2}) \\ &= 2y H_v - H_{v+1} \end{aligned} \quad (\text{AII.21})$$

$$\begin{aligned} \frac{d^2 H_v}{dy^2} &= 2H_v + 2y \frac{d}{dy} H_v - \frac{d}{dy} H_{v+1} \\ &= 2H_v + 2y (2y H_v - H_{v+1}) - (2y H_{v+1} - H_{v+2}) \\ &= 2(1 + 2y^2) H_v - 4y H_{v+1} + H_{v+2} \end{aligned} \quad (\text{AII.22})$$

The Hermite's equation is

$$\frac{d^2 H_v}{dy^2} - 2y \frac{dH_v}{dy} + \left( \frac{\lambda}{\alpha} - 1 \right) H_v = 0$$

Substituting  $\frac{\lambda}{\alpha} - 1 = 2v$ , we get

$$\frac{d^2 H_v}{dy^2} - 2y \frac{dH_v}{dy} + 2v H_v = 0$$

Substituting  $dH_v/dy$  and  $d^2 H_v/dy^2$  from Eqs (AII.21) and (AII.22), we get

$$[2(1 + 2y^2)H_v - 4y H_{v+1} + H_{v+2}] - 2y [2y H_v - H_{v+1}] + 2v H_v = 0$$

$$\text{or } H_{v+2} - 2y H_{v+1} + 2(v+1)H_v = 0$$

Replacing  $v$  by  $v-1$ , we get

$$H_{v+1} - 2y H_v + 2v H_{v-1} = 0 \quad (\text{AII.23})$$

Equation (AII.23) is the required recursion formula involving Hermite polynomials. Using this expression, one can generate the Hermite polynomials provided it is known that  $H_0 = 1$  and  $H_1 = 2y$ . For example, we have

$$\text{For } v=1 \quad H_2 - 2y H_1 + 2 \times 1 H_0 = 0 \quad \text{or } H_2 = 2y H_1 - 2H_0 = 4y^2 - 2$$

$$\begin{aligned} \text{For } v=2 \quad H_3 - 2y H_2 + 2 \times 2 H_1 &= 0 \quad \text{or } H_3 = 2y H_2 - 4H_1 = 2y(4y^2 - 2) - 4(2y) \\ &= 8y^3 - 12y. \end{aligned}$$

## THE FACTORIZATION METHOD

The factorization method can be applied to determine eigenvalues of a harmonic oscillator.

The Hamiltonian operator of a diatomic molecule executing harmonic oscillation is

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{k_f x^2}{2} \quad (\text{AII.24})$$

We divide the above expression by  $h\nu$  (where  $\nu = (1/2\pi)\sqrt{k_f/\mu}$ , a classical frequency of oscillation) to get a dimensionless Hamiltonian.

$$\begin{aligned} \hat{H} &= \frac{\hat{H}}{h\nu} = \frac{\hat{p}^2}{2\mu h\nu} + \frac{k_f x^2}{2h\nu} \\ &= \frac{\hat{p}^2}{2} + \frac{X^2}{2} \end{aligned} \quad (\text{AII.25})$$

$$\text{where } \hat{p}^2 = \frac{\hat{p}^2}{\mu h\nu} \quad \text{and} \quad X^2 = \frac{k_f x^2}{h\nu} = \alpha x^2 \quad (\text{AII.26})$$

The operator  $\hat{P}$  is given by the expression

$$\hat{P} = \frac{1}{\sqrt{\mu h\nu}} \left( \frac{h}{2\pi i} \frac{d}{dx} \right) \quad (\text{AII.27})$$

## Expression of Hamiltonian Operator

The differential  $dx$  is related to  $dX$  by the expression

$$dx = \sqrt{\frac{h\nu}{k_f}} dX \quad (\text{AII.28})$$

Replacing  $dx$  in terms of  $dX$  in Eq. (AII.27), we get

$$\hat{p} = \frac{1}{\sqrt{\mu h \nu}} \left( \frac{h}{2\pi i} \sqrt{\frac{k_f}{h \nu}} \cdot \frac{d}{dX} \right) = \frac{1}{i} \frac{d}{dX} \quad (\text{AII.29})$$

### Definition of the Ladder Operator

The ladder operator for harmonic oscillator is defined as

$$\hat{H}_+ = \hat{p} + iX \quad \text{and} \quad \hat{H}_- = \hat{p} - iX \quad (\text{AII.30})$$

We have

$$\begin{aligned} [\hat{p}, X] &= \hat{p}X - X\hat{p} \\ &= \frac{1}{i} \frac{d}{dX} X - X \left( \frac{1}{i} \frac{d}{dX} \right) = \frac{1}{i} \left( X \frac{d}{dX} + 1 \right) - X \left( \frac{1}{i} \frac{d}{dX} \right) \\ &= \frac{1}{i} = -i \end{aligned} \quad (\text{AII.31})^\dagger$$

### Commutator of $\hat{H}_\pm$ and $X$

We have

$$\begin{aligned} [\hat{H}_\pm, X] &= \hat{H}_\pm X - X\hat{H}_\pm = (\hat{p} \pm iX)X - X(\hat{p} \pm iX) \\ &= \hat{p}X \pm iX^2 - X\hat{p} \mp iX^2 = \hat{p}X - X\hat{p} \\ &= -i \end{aligned} \quad (\text{AII.32})$$

We have

$$\begin{aligned} [\hat{H}_\pm, \hat{H}] &= \hat{H}_\pm \hat{H} - \hat{H} \hat{H}_\pm \\ &= (\hat{p} \pm iX) \left( \frac{\hat{p}^2}{2} + \frac{X^2}{2} \right) - \left( \frac{\hat{p}^2}{2} + \frac{X^2}{2} \right) (\hat{p} \pm iX) \\ &= \frac{1}{2} [(\hat{p}^3 \pm \hat{p}X^2 \pm iX\hat{p}^2 \pm iX^3) - (\hat{p}^3 \pm i\hat{p}^2X + X^2\hat{p} \pm iX^3)] \\ &= \frac{1}{2} [(\hat{p}X^2 - X^2\hat{p}) \pm i(X\hat{p}^2 - \hat{p}^2X)] \end{aligned} \quad (\text{AII.33})$$

$$\begin{aligned} \text{Now } \hat{p}X^2 - X^2\hat{p} &= \left( \frac{1}{i} \frac{d}{dX} \right) X^2 - X^2 \left( \frac{1}{i} \frac{d}{dX} \right) = \frac{1}{i} \left( X^2 \frac{d}{dX} + 2X \right) - X^2 \left( \frac{1}{i} \frac{d}{dX} \right) \\ &= \frac{2X}{i} = -2iX \end{aligned} \quad (\text{AII.34})^\ddagger$$

$$\begin{aligned} + \left( \frac{d}{dX} \right) X &\equiv \frac{d}{dX} (Xf) = X \frac{df}{dX} + f \equiv X \frac{d}{dX} + 1 \\ \ddagger \frac{d^2}{dX^2} X^2 &\equiv \frac{d}{dX} (X^2 f) = X^2 \frac{df}{dX} + f(2X) \equiv X^2 \frac{d}{dX} + 2X \end{aligned}$$

$$\begin{aligned} X\hat{p}^2 - \hat{p}^2X &= X \left( \frac{1}{i} \frac{d}{dX} \right)^2 - \left( \frac{1}{i} \frac{d}{dX} \right)^2 X \\ &= -X \frac{d^2}{dX^2} + \left( X \frac{d^2}{dX^2} + \frac{d}{dX} + \frac{d}{dX} \right) \\ &= 2 \frac{d}{dX} = 2i \left( \frac{1}{i} \frac{d}{dX} \right) = 2i\hat{p} \end{aligned} \quad (\text{AII.35})^\dagger$$

Substituting Eqs (AII.34) and (AII.35) in Eq. (AII.33), we get

$$\begin{aligned} [\hat{H}_\pm, \hat{H}] &= \frac{1}{2} [-2iX \pm 2i\hat{p}^2] = \mp i\hat{p} - iX \\ &= \mp(\hat{p} \pm iX) = \mp \hat{H}_\pm \end{aligned} \quad (\text{AII.36})$$

The Schrödinger equation of the harmonic oscillator is

$$\hat{H}\psi = E\psi$$

Dividing by  $h\nu$ , we get

$$\frac{\hat{H}}{h\nu} \psi = \frac{E}{h\nu} \psi \quad \text{i.e.} \quad \hat{H}\psi = E\psi \quad (\text{AII.37})$$

Operating Eq. (AII.37) by  $\hat{H}_\pm$ , we get

$$\hat{H}_\pm(\hat{H}\psi) = \hat{H}_\pm(E\psi)$$

which on using Eq. (AII.36) becomes

$$\begin{aligned} (\hat{H}\hat{H}_\pm \mp \hat{H}_\pm \hat{H})\psi &= E(\hat{H}_\pm \psi) \\ \hat{H}(\hat{H}_\pm \psi) &= (E \pm 1)(\hat{H}_\pm \psi) \end{aligned} \quad (\text{AII.38})$$

i.e.

that is, the function  $\hat{H}_\pm \psi$  is also an eigenfunction of  $\hat{H}$  with an eigenvalue one higher or lower than the eigenvalue of  $\psi$ .

Continuing operation by  $\hat{H}_\pm$  would give

$$\begin{aligned} \hat{H}_\pm^k(\hat{H}\psi) &= \hat{H}_\pm^k(E\psi) \\ \hat{H}(\hat{H}_\pm^k \psi) &= (E + k)(\hat{H}_\pm^k \psi); \quad k = 0, 1, 2, 3, \dots \end{aligned} \quad (\text{AII.39})$$

Since both the kinetic and the potential energies are positive, no eigenvalue of  $\hat{H}$  will be less than zero. This implies that there will be a lower limit of energy. Let it be  $E_0$  and the corresponding wave function for this energy be  $\psi_0$ .

$$\frac{d^2}{dX^2} X = \frac{d}{dX} \left( \frac{d}{dX} Xf \right) = \frac{d}{dX} \left( X \frac{df}{dX} + f \right) = X \frac{d^2 f}{dX^2} + \frac{df}{dX} + \frac{df}{dX} \equiv X \frac{d^2}{dX^2} + 2 \frac{d}{dX}$$

The application of  $\hat{H}_-$  on  $\psi_0$  will be equal to zero as there is no state function lower than  $\psi_0$ , i.e.

$$\hat{H}_- \psi_0 = 0 \quad (\text{AII.40})$$

Operating  $H_+$  on Eq. (AII.40), we get

$$\hat{H}_+ \hat{H}_- \psi_0 = 0$$

Substituting the expressions of  $H_+$  and  $H_-$ , we get

$$(\hat{P} + iX)(\hat{P} - iX)\psi_0 = 0$$

$$\text{or } (\hat{P}^2 - i\hat{P}X + iX\hat{P} + X^2)\psi_0 = 0$$

$$\text{or } [(\hat{P}^2 + X^2) - i(\hat{P}X - X\hat{P})]\psi_0 = 0 \quad \text{or } [2\hat{H} - i(-i)]\psi_0 = 0$$

$$\text{or } 2\hat{H}\psi_0 - (1)\psi_0 = 0 \quad \text{or } (2E_0 - 1)\psi_0 = 0$$

$$\text{This gives } E_0 = \frac{1}{2}$$

The eigenvalue corresponding to the Hamiltonian  $\hat{H}$  will be

$$E'_0 = \frac{1}{2} h\nu \quad (\text{AII.41})$$

The remaining eigenvalues of  $\hat{H}$  increases by steps of one (Eq. AII.39), i.e.

$$E'_v = \left(v + \frac{1}{2}\right) h\nu; \quad v = 0, 1, 2, 3, \dots \quad (\text{AII.42})$$

The ground-state wave function may be obtained by the expression

$$\hat{H}_- \psi_0 = 0 \quad \text{i.e. } (\hat{P} - iX)\psi_0 = 0$$

Substituting the expression of  $\hat{P}$  from Eq. (AII.29), we get

$$\left(\frac{1}{i} \frac{d}{dX} - iX\right)\psi_0 = 0 \quad \text{or } \frac{d\psi_0}{dX} = -X\psi_0$$

$$\text{i.e. } \frac{d\psi_0}{\psi_0} = -XdX$$

which on integration gives

$$\ln \psi_0 = -\frac{X^2}{2} + \text{constant} \quad \text{or } \psi_0 = A \exp(-X^2/2) \quad (\text{AII.43})$$

The constant  $A$  may be determined from the normalization of wave function, which gives

$$A^2 \int_{-\infty}^{+\infty} \psi_0^2 dX = 2A^2 \int_0^{\infty} e^{-X^2} dX = (2A^2) \left(\frac{\pi}{4}\right)^{1/2} = A^2 (\pi)^{1/2} = 1$$

$$\text{i.e. } A = (1/\pi)^{1/4} \quad (\text{AII.44})$$

The higher wave functions may be determined from  $\psi_0$  by using the expression

$$\psi_k = \hat{H}_+^k \psi_0 \quad (\text{AII.45})$$

For example, for  $k = 1$  we have

$$\begin{aligned} \psi_1 &= \hat{H}_+ \psi_0 = (\hat{P} + iX)\psi_0 \\ &= \left(\frac{1}{i} \frac{d}{dX} + iX\right)\psi_0 = \left(\frac{1}{i} \frac{d}{dX} + iX\right)(Ae^{-X^2/2}) \\ &= Ai \left[-\frac{d}{dX} e^{-X^2/2} + Xe^{-X^2/2}\right] = Ai[-(-X)e^{-X^2/2} + Xe^{-X^2/2}] \\ &= i(2X)(Ae^{-X^2/2}) \end{aligned} \quad (\text{AII.46})$$

For  $k = 2$ , we have

$$\begin{aligned} \hat{H}_+^2 \psi_0 &= \hat{H}_+ (\hat{H}_+ \psi_0) = (\hat{P} + iX)[2iXAe^{-X^2/2}] \\ &= \left[\frac{1}{i} \frac{d}{dX} + iX\right][2iXAe^{-X^2/2}] \\ &= -2A \left[-\frac{d}{dX} (Xe^{-X^2/2}) + X^2 e^{-X^2/2}\right] \\ &= -2A[-e^{-X^2/2} + X^2 e^{-X^2/2} + X^2 e^{-X^2/2}] \\ &= -A(4X^2 - 2)e^{-X^2/2} \end{aligned} \quad (\text{AII.47})$$

In general, the wave functions of a harmonic oscillator is given by the expression

$$\psi_v = \left(\frac{\sqrt{\alpha}}{2^v v!}\right)^{1/2} \left[\exp\left(-\frac{X^2}{2}\right)\right] H_v \quad (\text{AII.48})$$

where  $\alpha = k_e/h\nu$ . The function  $H_v$  is known as Hermite polynomials. The values of a few Hermite polynomials are as follows.

$$\begin{aligned} H_0 &= 1; & H_1 &= 2X; & H_2 &= 4X^2 - 2; \\ H_3 &= 8X^3 - 12X; & H_4 &= 16X^4 - 48X^2 + 12 \\ &\text{and so on.} \end{aligned}$$

### ANNEXURE III Operators for the Components of Angular Momentum

#### Definition of Angular Momentum

The expression of angular momentum of a single particle revolving around a fixed point is given by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \quad (\text{AIII.1})$$

where  $\mathbf{r}$  is the radius vector from the fixed point to the particle and  $\mathbf{p}$  is its linear momentum vector.

#### Expressions of Components of Angular Momentum

In terms of Cartesian coordinates, we can write

$$\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$$

and  $\mathbf{p} = p_x\mathbf{i} + p_y\mathbf{j} + p_z\mathbf{k}$

$$\begin{aligned} \text{Hence, } \mathbf{L} = \mathbf{r} \times \mathbf{p} &= (xi + yj + zk) \times (p_x\mathbf{i} + p_y\mathbf{j} + p_z\mathbf{k}) \\ &= xp_x(\mathbf{i} \times \mathbf{i}) + xp_y(\mathbf{i} \times \mathbf{j}) + xp_z(\mathbf{i} \times \mathbf{k}) \\ &\quad + yp_x(\mathbf{j} \times \mathbf{i}) + yp_y(\mathbf{j} \times \mathbf{j}) + yp_z(\mathbf{j} \times \mathbf{k}) \\ &\quad + zp_x(\mathbf{k} \times \mathbf{i}) + zp_y(\mathbf{k} \times \mathbf{j}) + zp_z(\mathbf{k} \times \mathbf{k}) \end{aligned}$$

Keeping in mind that

$$\mathbf{i} \times \mathbf{i} = 0 ; \quad \mathbf{j} \times \mathbf{j} = 0 \quad \text{and} \quad \mathbf{k} \times \mathbf{k} = 0$$

$$\mathbf{i} \times \mathbf{j} = \mathbf{k} ; \quad \mathbf{j} \times \mathbf{k} = \mathbf{i} \quad \text{and} \quad \mathbf{k} \times \mathbf{i} = \mathbf{j}$$

and  $\mathbf{j} \times \mathbf{i} = -\mathbf{k} ; \quad \mathbf{k} \times \mathbf{j} = -\mathbf{i} \quad \text{and} \quad \mathbf{i} \times \mathbf{k} = -\mathbf{j}$

$$\begin{aligned} \text{we get } \mathbf{L} &= xp_y\mathbf{k} - xp_z\mathbf{j} - yp_z\mathbf{i} + zp_x\mathbf{j} - zp_y\mathbf{i} \\ &= (yp_z - zp_y)\mathbf{i} + (zp_x - xp_z)\mathbf{j} + (xp_y - yp_x)\mathbf{k} \end{aligned}$$

Since  $\mathbf{L} = L_x\mathbf{i} + L_y\mathbf{j} + L_z\mathbf{k}$ , we get

$$L_x = yp_z - zp_y \quad (\text{AIII.2})$$

$$L_y = zp_x - xp_z \quad (\text{AIII.3})$$

$$L_z = xp_y - yp_x \quad (\text{AIII.4})$$

**Note:** The above expressions of components of angular momentum can be derived by using the determinant notation

$$\mathbf{r} \times \mathbf{p} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

#### Angular Momentum Operators in Cartesian Coordinates

Replacing  $p_x$ ,  $p_y$  and  $p_z$  in Eqs (AIII.2)–(AIII.4) by the corresponding operators we get the operators (represented by the symbol of physical quantity with overhead cap of  $L_x$ ,  $L_y$  and  $L_z$ ).

$$\hat{L}_x = y \left( \frac{h}{2\pi i} \frac{\partial}{\partial z} \right) - z \left( \frac{h}{2\pi i} \frac{\partial}{\partial y} \right) = \frac{h}{2\pi i} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \quad (\text{AIII.5})$$

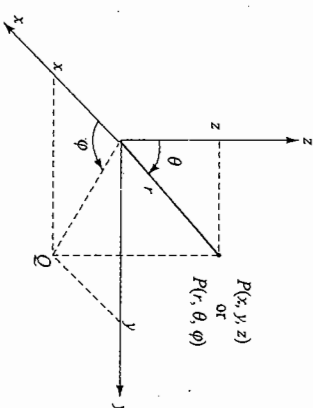
$$\hat{L}_y = z \left( \frac{h}{2\pi i} \frac{\partial}{\partial x} \right) - x \left( \frac{h}{2\pi i} \frac{\partial}{\partial z} \right) = \frac{h}{2\pi i} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \quad (\text{AIII.6})$$

$$\hat{L}_z = x \left( \frac{h}{2\pi i} \frac{\partial}{\partial y} \right) - y \left( \frac{h}{2\pi i} \frac{\partial}{\partial x} \right) = \frac{h}{2\pi i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad (\text{AIII.7})$$

#### Angular Momentum Operators in Spherical Polar Coordinates

The cartesian coordinates ( $x$ ,  $y$ ,  $z$ ) of a point are related to its spherical polar coordinates ( $r$ ,  $\theta$ ,  $\phi$ ) by the expressions

$$\begin{aligned} z &= r \cos \theta \\ x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \end{aligned}$$



The transformations from Cartesian coordinates to spherical polar coordinates can be carried over by using the expressions

$$\frac{\partial}{\partial x} = \left( \frac{\partial r}{\partial x} \right) \frac{\partial}{\partial r} + \left( \frac{\partial \theta}{\partial x} \right) \frac{\partial}{\partial \theta} + \left( \frac{\partial \phi}{\partial x} \right) \frac{\partial}{\partial \phi} \quad (\text{AIII.8})$$

$$\frac{\partial}{\partial y} = \left( \frac{\partial r}{\partial y} \right) \frac{\partial}{\partial r} + \left( \frac{\partial \theta}{\partial y} \right) \frac{\partial}{\partial \theta} + \left( \frac{\partial \phi}{\partial y} \right) \frac{\partial}{\partial \phi} \quad (\text{AIII.9})$$

$$\frac{\partial}{\partial z} = \left( \frac{\partial r}{\partial z} \right) \frac{\partial}{\partial r} + \left( \frac{\partial \theta}{\partial z} \right) \frac{\partial}{\partial \theta} + \left( \frac{\partial \phi}{\partial z} \right) \frac{\partial}{\partial \phi} \quad (\text{AIII.10})$$

Using the fact that  $r^2 = x^2 + y^2 + z^2$ , we get

$$(i) \quad \frac{\partial r}{\partial x} = \frac{x}{r} = \frac{r \sin \theta \cos \phi}{r} = \sin \theta \cos \phi$$

$$(ii) \quad \frac{\partial r}{\partial y} = \frac{y}{r} = \frac{r \sin \theta \sin \phi}{r} = \sin \theta \sin \phi$$

$$(iii) \quad \frac{\partial r}{\partial z} = \frac{z}{r} = \frac{r \cos \theta}{r} = \cos \theta$$



From the expression  $\cos \theta = \frac{z}{r} = \frac{z}{(x^2 + y^2 + z^2)^{1/2}}$ , we get

$$(iv) \quad -\sin \theta \frac{\partial \theta}{\partial x} = -\frac{1}{2} \frac{z}{(x^2 + y^2 + z^2)^{3/2}} \quad (2x)$$

$$\text{i.e.} \quad \frac{\partial \theta}{\partial x} = \frac{zx}{\sin \theta (x^2 + y^2 + z^2)^{3/2}} = \frac{(r \cos \theta)(r \sin \theta \cos \varphi)}{(\sin \theta)r^3} = \frac{\cos \theta \cos \varphi}{r}$$

$$(v) \quad -\sin \theta \frac{\partial \theta}{\partial y} = -\frac{1}{2} \frac{z}{(x^2 + y^2 + z^2)^{3/2}} \quad (2y)$$

$$\text{i.e.} \quad \frac{\partial \theta}{\partial y} = \frac{zy}{\sin \theta (x^2 + y^2 + z^2)^{3/2}} = \frac{(r \cos \theta)(r \sin \theta \sin \varphi)}{(\sin \theta)r^3} = \frac{\cos \theta \sin \varphi}{r}$$

$$(vi) \quad -\sin \theta \frac{\partial \theta}{\partial z} = \frac{1}{(x^2 + y^2 + z^2)^{1/2}} + \left(-\frac{1}{2}\right) \frac{z}{(x^2 + y^2 + z^2)^{3/2}} \quad (2z)$$

$$\text{i.e.} \quad \frac{\partial \theta}{\partial z} = \left(-\frac{1}{\sin \theta}\right) \left(\frac{1}{r} - \frac{r^2 \cos^2 \theta}{r^3}\right) = \left(-\frac{1}{\sin \theta}\right) \left(\frac{1}{r}\right) (1 - \cos^2 \theta)$$

$$= -\frac{\sin \theta}{r}$$

Finally, from the expression  $\tan \varphi = y/x$ , we get

$$(vii) \quad \sec^2 \varphi \frac{\partial \varphi}{\partial x} = -\frac{y}{x^2}$$

$$\text{i.e.} \quad \frac{\partial \varphi}{\partial x} = -\left(\frac{1}{\sec^2 \varphi}\right) \left(\frac{y}{x^2}\right) = -(\cos^2 \varphi) \left(\frac{r \sin \theta \sin \varphi}{r^2 \sin^2 \theta \cos^2 \varphi}\right) = -\frac{\sin \varphi}{r \sin \theta}$$

$$(ix) \quad \sec^2 \varphi \frac{\partial \varphi}{\partial y} = \frac{1}{x}$$

$$\text{i.e.} \quad \frac{\partial \varphi}{\partial y} = \left(\frac{1}{\sec^2 \varphi}\right) \left(\frac{1}{x}\right) = (\cos^2 \varphi) \left(\frac{1}{r \sin \theta \cos \varphi}\right) = \frac{\cos \varphi}{r \sin \theta}$$

$$(x) \quad \frac{\partial \varphi}{\partial z} = 0$$

With these derivatives, Eqs (AII.8) – (AII.10) become

$$\begin{aligned} \frac{\partial}{\partial x} &= \left(\frac{\partial r}{\partial x}\right) \frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial x}\right) \left(\frac{\partial}{\partial \theta}\right) + \left(\frac{\partial \varphi}{\partial x}\right) \frac{\partial}{\partial \varphi} \\ &= (\sin \theta \cos \varphi) \frac{\partial}{\partial r} + \left(\frac{\cos \theta \cos \varphi}{r}\right) \frac{\partial}{\partial \theta} + \left(-\frac{\sin \varphi}{r \sin \theta}\right) \frac{\partial}{\partial \varphi} \quad (\text{AIII.11}) \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial y} &= \left(\frac{\partial r}{\partial y}\right) \left(\frac{\partial}{\partial r}\right) + \left(\frac{\partial \theta}{\partial y}\right) \left(\frac{\partial}{\partial \theta}\right) + \left(\frac{\partial \varphi}{\partial y}\right) \left(\frac{\partial}{\partial \varphi}\right) \\ &= (\sin \theta \sin \varphi) \frac{\partial}{\partial r} + \left(\frac{\cos \theta \sin \varphi}{r}\right) \frac{\partial}{\partial \theta} + \left(\frac{\cos \varphi}{r \sin \theta}\right) \frac{\partial}{\partial \varphi} \quad (\text{AIII.12}) \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial z} &= \left(\frac{\partial r}{\partial z}\right) \frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial z}\right) \frac{\partial}{\partial \theta} + \left(\frac{\partial \varphi}{\partial z}\right) \frac{\partial}{\partial \varphi} \\ &= (\cos \theta) \frac{\partial}{\partial r} + \left(-\frac{\sin \theta}{r}\right) \frac{\partial}{\partial \theta} \quad (\text{AIII.13}) \end{aligned}$$

We have

$$\begin{aligned} \hat{L}_x &= \frac{h}{2\pi i} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ &= \frac{h}{2\pi i} \left[ (r \sin \theta \sin \varphi) \left( \cos \theta \frac{\partial}{\partial r} - \frac{\sin \theta}{r} \frac{\partial}{\partial \theta} \right) \right. \\ &\quad \left. - (r \cos \theta) \left( \sin \theta \sin \varphi \frac{\partial}{\partial r} + \frac{\cos \theta \sin \varphi}{r} \frac{\partial}{\partial \theta} + \frac{\cos \varphi}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) \right] \\ &= \frac{h}{2\pi i} \left[ (-\sin^2 \theta \sin \varphi - \cos^2 \theta \sin \varphi) \frac{\partial}{\partial \theta} - \frac{\cos \theta \cos \varphi}{\sin \theta} \frac{\partial}{\partial \varphi} \right] \\ &= -\frac{h}{2\pi i} \left( \sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \quad (\text{AIII.14}) \end{aligned}$$

We have

$$\begin{aligned} \hat{L}_y &= \frac{h}{2\pi i} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ &= \frac{h}{2\pi i} \left[ (r \cos \theta) \left( \sin \theta \cos \varphi \frac{\partial}{\partial r} + \frac{\cos \theta \cos \varphi}{r} \frac{\partial}{\partial \theta} - \frac{\sin \varphi}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) \right. \\ &\quad \left. - (r \sin \theta \cos \varphi) \left( \cos \theta \frac{\partial}{\partial r} - \frac{\sin \theta}{r} \frac{\partial}{\partial \theta} \right) \right] \\ &= \frac{h}{2\pi i} \left[ (\cos^2 \theta \cos \varphi + \sin^2 \theta \cos \varphi) \frac{\partial}{\partial \theta} - \frac{\cos \theta \sin \varphi}{\sin \theta} \frac{\partial}{\partial \varphi} \right] \\ &= \frac{h}{2\pi i} \left( \cos \varphi \frac{\partial}{\partial \theta} - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \quad (\text{AIII.15}) \end{aligned}$$

We know

$$\hat{L}_z = \frac{h}{2\pi i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

$$\begin{aligned}
&= \frac{h}{2\pi i} \left[ (r \sin \theta \cos \varphi) \left( \sin \theta \sin \varphi \frac{\partial}{\partial r} + \frac{\cos \theta \sin \varphi}{r} \frac{\partial}{\partial \theta} + \frac{\cos \varphi}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) \right. \\
&\quad \left. - (r \sin \theta \sin \varphi) \left( \sin \theta \cos \varphi \frac{\partial}{\partial r} + \frac{\cos \theta \cos \varphi}{r} \frac{\partial}{\partial \theta} - \frac{\sin \varphi}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) \right] \\
&= \frac{h}{2\pi i} \left[ (\cos^2 \varphi + \sin^2 \varphi) \frac{\partial}{\partial \varphi} \right] \\
&= \frac{h}{2\pi i} \frac{\partial}{\partial \varphi} \quad (\text{AIII.16})
\end{aligned}$$

### Operator for the Square of Angular Momentum

The square of angular momentum is defined as the scalar product of the angular momentum vector with itself, i.e.

$$L^2 = L \cdot L$$

In terms of components, we have

$$L^2 = (L_x i + L_y j + L_z k) \cdot (L_x i + L_y j + L_z k)$$

Using the fact that  $i \cdot j = \delta_{ij}$  (where  $\delta_{ij} = 1$  if  $i = j$  and  $\delta_{ij} = 0$  if  $i \neq j$ ), we get

$$L^2 = L_x^2 + L_y^2 + L_z^2 \quad (\text{AIII.17})$$

The operator for  $L^2$  is

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \quad (\text{AIII.18})$$

### Expression of $\hat{L}_x^2$

We have

$$\begin{aligned}
\hat{L}_x^2 &= \hat{L}_x \hat{L}_x = \left[ -\frac{h}{2\pi i} \left( \sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \right] \\
&\quad \left[ -\frac{h}{2\pi i} \left( \sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \right] \\
&= -\frac{h^2}{4\pi^2} \left[ \sin \varphi \frac{\partial}{\partial \theta} \left( \sin \varphi \frac{\partial}{\partial \theta} \right) + \sin \varphi \frac{\partial}{\partial \theta} \left( \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \right. \\
&\quad \left. + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \left( \sin \varphi \frac{\partial}{\partial \theta} \right) + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \left( \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \right] \\
&= -\frac{h^2}{4\pi^2} \left[ \sin^2 \varphi \frac{\partial^2}{\partial \theta^2} + \sin \varphi \cos \varphi \left\{ \frac{\partial}{\partial \theta} (\cot \theta) \frac{\partial}{\partial \varphi} + \cot \theta \frac{\partial^2}{\partial \theta \partial \varphi} \right\} \right. \\
&\quad \left. + \cot \theta \cos \varphi \left\{ \frac{\partial}{\partial \varphi} (\sin \varphi) \frac{\partial}{\partial \theta} + \sin \varphi \frac{\partial^2}{\partial \varphi \partial \theta} \right\} \right. \\
&\quad \left. + \cot \theta \cos \varphi \cot \theta \left\{ \frac{\partial}{\partial \varphi} (\cos \varphi) \frac{\partial}{\partial \varphi} + \cos \varphi \frac{\partial^2}{\partial \varphi^2} \right\} \right]
\end{aligned}$$

$$\begin{aligned}
&= -\frac{h^2}{4\pi^2} \left[ \sin^2 \varphi \frac{\partial^2}{\partial \theta^2} - \sin \varphi \cos \varphi \operatorname{cosec}^2 \theta \frac{\partial}{\partial \varphi} \right. \\
&\quad \left. + \sin \varphi \cos \varphi \cot \theta \frac{\partial^2}{\partial \theta \partial \varphi} + \cot \theta \cos^2 \varphi \frac{\partial}{\partial \theta} \right. \\
&\quad \left. + \cot \theta \cos \varphi \sin \varphi \frac{\partial^2}{\partial \varphi \partial \theta} - \cot^2 \theta \cos \varphi \sin \varphi \frac{\partial}{\partial \varphi} \right. \\
&\quad \left. + \cot^2 \theta \cos^2 \varphi \frac{\partial^2}{\partial \varphi^2} \right] \quad (\text{AIII.19})
\end{aligned}$$

### Expression of $\hat{L}_y^2$

We have

$$\begin{aligned}
\hat{L}_y^2 &= \hat{L}_y \hat{L}_y = \left[ \frac{h}{2\pi i} \left( \cos \varphi \frac{\partial}{\partial \theta} - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \right] \\
&\quad \left[ \frac{h}{2\pi i} \left( \cos \varphi \frac{\partial}{\partial \theta} - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \right] \\
&= -\frac{h^2}{4\pi^2} \left[ \cos \varphi \frac{\partial}{\partial \theta} \left( \cos \varphi \frac{\partial}{\partial \theta} \right) + \cos \varphi \frac{\partial}{\partial \theta} \left( -\cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \right. \\
&\quad \left. - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \left( \cos \varphi \frac{\partial}{\partial \theta} \right) - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \left( -\cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \right] \\
&= -\frac{h^2}{4\pi^2} \left[ \cos^2 \varphi \frac{\partial^2}{\partial \theta^2} - \cos \varphi \sin \varphi \left\{ \frac{\partial}{\partial \theta} (\cot \theta) \frac{\partial}{\partial \varphi} + \cot \theta \frac{\partial^2}{\partial \theta \partial \varphi} \right\} \right. \\
&\quad \left. - \cot \theta \sin \varphi \left\{ \frac{\partial}{\partial \varphi} (\cos \varphi) \frac{\partial}{\partial \theta} + \cos \varphi \frac{\partial^2}{\partial \varphi \partial \theta} \right\} \right. \\
&\quad \left. + \cot^2 \theta \sin \varphi \left\{ \frac{\partial}{\partial \varphi} (\sin \varphi) \frac{\partial}{\partial \varphi} + \sin \varphi \frac{\partial^2}{\partial \varphi^2} \right\} \right] \\
&= -\frac{h^2}{4\pi^2} \left[ \cos^2 \varphi \frac{\partial^2}{\partial \theta^2} + \cos \varphi \sin \varphi \operatorname{cosec}^2 \theta \frac{\partial}{\partial \varphi} \right. \\
&\quad \left. - \cos \varphi \sin \varphi \cot \theta \frac{\partial^2}{\partial \theta \partial \varphi} + \cot \theta \sin^2 \varphi \frac{\partial}{\partial \theta} \right. \\
&\quad \left. - \cot \theta \sin \varphi \cos \varphi \frac{\partial^2}{\partial \varphi \partial \theta} + \cot^2 \theta \sin \varphi \cos \varphi \frac{\partial}{\partial \varphi} \right. \\
&\quad \left. + \cot^2 \theta \sin^2 \varphi \frac{\partial^2}{\partial \varphi^2} \right] \quad (\text{AIII.20})
\end{aligned}$$

### Expression of $\hat{L}_z^2$

We have

$$\hat{L}_z^2 = \hat{L}_z \hat{L}_z = \left( \frac{h}{2\pi i} \frac{\partial}{\partial \varphi} \right) \left( \frac{h}{2\pi i} \frac{\partial}{\partial \varphi} \right) = -\frac{h^2}{4\pi^2} \frac{\partial^2}{\partial \varphi^2} \quad (\text{AIII.21})$$

Expression of  $\hat{L}^2$ 

We have

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

Writing  $\hat{L}_x$  and  $\hat{L}_y$  together, we get

(AIII.22)

$$\hat{L}^2 = -\frac{h^2}{4\pi^2} \left[ (\sin^2 \varphi + \cos^2 \varphi) \frac{\partial^2}{\partial \theta^2} + \cot \theta (\sin^2 \varphi + \cos^2 \varphi) \frac{\partial}{\partial \varphi} \right. \\ \left. + \cot^2 \theta (\sin^2 \varphi + \cos^2 \varphi) \frac{\partial^2}{\partial \varphi^2} \right] - \frac{h^2}{4\pi^2} \frac{\partial^2}{\partial \varphi^2}$$

$$= -\frac{h^2}{4\pi^2} \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + (\cot^2 \theta + 1) \frac{\partial^2}{\partial \varphi^2} \right]$$

$$= -\frac{h^2}{4\pi^2} \left[ \frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \theta} + \operatorname{cosec}^2 \theta \frac{\partial^2}{\partial \varphi^2} \right]$$

$$= -\frac{h^2}{4\pi^2} \left[ \frac{1}{\sin \theta} \left( \sin \theta \frac{\partial^2}{\partial \theta^2} + \cos \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]$$

$$= -\frac{h^2}{4\pi^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]$$

(AIII.23)

## Commutators of Angular Momentum Operators

## ANNEXURE IV

## Definition of Commutator

The commutator of two operators  $\hat{\alpha}$  and  $\hat{\beta}$  is an operator defined as  $\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha}$ . This is usually written as  $[\hat{\alpha}, \hat{\beta}]$ .

The two operators  $\hat{\alpha}$  and  $\hat{\beta}$  are said to commute each other if their commutator is equal to zero, i.e.

$$[\hat{\alpha}, \hat{\beta}] = \hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha} = 0 \quad (\text{AIV.1})$$

If the commutator is not equal to zero, the two operators are said to be non-commuting, i.e.

$$[\hat{\alpha}, \hat{\beta}] = \hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha} \neq 0 \quad (\text{AIV.2})$$

In the above definitions of commuting and noncommuting operators, it is implicit that these operators operate on an arbitrary function, say  $f$ . If

$$\hat{\alpha}\hat{\beta}f = \hat{\beta}\hat{\alpha}f \quad \text{for all functions } f,$$

then  $\hat{\alpha}$  and  $\hat{\beta}$  commute with each other and if

$$\hat{\alpha}\hat{\beta}f \neq \hat{\beta}\hat{\alpha}f \quad \text{for all function } f,$$

then  $\hat{\alpha}$  and  $\hat{\beta}$  do not commute with each other.

To be specific, let  $\hat{\alpha} = d/dx$  and  $\hat{\beta} = x$ . Then

$$\hat{\alpha}\hat{\beta}f = \left( \frac{d}{dx} \right) (xf) = \frac{d}{dx} \left( x \frac{df}{dx} + f \right)$$

$$\hat{\beta}\hat{\alpha}f = (x) \left( \frac{d}{dx} \right) f = x \left( \frac{df}{dx} \right)$$

$$\text{Hence } \hat{\alpha}\hat{\beta}f - \hat{\beta}\hat{\alpha}f = f \quad \text{i.e. } (\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha})f = \hat{I}f; \quad (\text{where } \hat{I} = \text{unit operator})$$

Thus, the operators  $x$  and  $d/dx$  do not commute with each other.

If two operators  $\hat{\alpha}$  and  $\hat{\beta}$  commute, then there exists a set of functions which are simultaneously eigenfunctions of both the operators.

A simple proof of the above statement is as follows.

Let  $\psi_i$  be an eigenfunction of the operator  $\hat{\alpha}$ . Hence, we can write

$$\hat{\alpha}\psi_i = a_i \psi_i$$

## Eigenfunction of Commuting Operators

Let the operator  $\hat{\beta}$  commute with the operator  $\hat{\alpha}$ . Since  $\hat{\alpha}$  and  $\hat{\beta}$  commute we can write

$$\begin{aligned}\hat{\alpha}\hat{\beta}\psi_i &= \hat{\beta}\hat{\alpha}\psi_i = \hat{\beta}(a_i\psi_i) = a_i(\hat{\beta}\psi_i) \\ \text{i.e.} \quad \hat{\alpha}(\hat{\beta}\psi_i) &= a_i(\hat{\beta}\psi_i)\end{aligned}$$

This means that  $\hat{\beta}\psi_i$  is also an eigenfunction of the operator  $\hat{\alpha}$  and its eigenvalue  $a_i$  is the same as that of the function  $\psi_i$ . This is possible only when  $\hat{\beta}\psi_i$  is a multiple of  $\psi_i$ , say  $b_i\psi_i$ , where  $b_i$  is a constant, i.e.

$$\hat{\beta}\psi_i = b_i\psi_i$$

This equation implies that  $\psi_i$  is also an eigenfunction of  $\hat{\beta}$  with eigenvalue  $b_i$ .

The converse of the above fact may be stated as follows.

If there exists a set of functions  $\psi_1, \psi_2, \psi_3, \dots, \psi_i$  which are eigenfunctions of two operators  $\hat{\alpha}$  and  $\hat{\beta}$ , then these two operators commute.

This converse fact may be proved as follows.

Let  $\psi_i$  be an eigenfunction of the operators  $\hat{\alpha}$  and  $\hat{\beta}$  with eigenvalues  $a_i$  and  $b_i$  respectively. We can write

$$\hat{\alpha}\psi_i = a_i\psi_i \quad \text{and} \quad \hat{\beta}\psi_i = b_i\psi_i$$

Now

$$\begin{aligned}\hat{\alpha}\hat{\beta}\psi_i &= \hat{\alpha}(b_i\psi_i) = b_i(\hat{\alpha}\psi_i) = b_ia_i\psi_i \\ \hat{\beta}\hat{\alpha}\psi_i &= \hat{\beta}(a_i\psi_i) = a_i(\hat{\beta}\psi_i) = a_ib_i\psi_i\end{aligned}$$

From these expressions, it follows that

$$\hat{\alpha}\hat{\beta}\psi_i - \hat{\beta}\hat{\alpha}\psi_i = 0 \quad \text{or} \quad (\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha})\psi_i = 0$$

that is the commutator of  $\hat{\alpha}$  and  $\hat{\beta}$  is zero. This implies that the operators  $\hat{\alpha}$  and  $\hat{\beta}$  commute.

We know that

- (i) The eigenvalue of a Hermitian operator is real.
- (ii) A real eigenvalue implies that the physical quantity for which the operator stands for can be measured experimentally.
- (iii) The eigenvalues of two commuting operators can be computed by using the common set of eigenfunctions.

From these facts, it follows that

If the two operators commute, then it is possible to measure simultaneously the precise values of both the physical quantities for which operators stand for

If the two operators do not commute, then it is not possible to measure simultaneously the precise values of both the physical quantities for which operators stand for.

The operator of  $P_x$  is  $(\hbar/2\pi i)(d/dx)$ .

Hence

$$\hat{P}_x \hat{P}_x f = (x) \left( \frac{\hbar}{2\pi i} \frac{d}{dx} \right) f = \frac{\hbar}{2\pi i} x \frac{df}{dx}$$

$$\hat{P}_x \hat{x} f = \left( \frac{\hbar}{2\pi i} \frac{d}{dx} \right) (x) f = \frac{\hbar}{2\pi i} \frac{d}{dx} (xf) = \frac{\hbar x}{2\pi i} \frac{df}{dx} + \frac{\hbar}{2\pi i} f$$

$$\begin{aligned}[\hat{P}_x, \hat{x}] f &= \hat{P}_x \hat{x} f - \hat{x} \hat{P}_x f \\ &= \left( \frac{\hbar x}{2\pi i} \frac{df}{dx} + \frac{\hbar}{2\pi i} f \right) - \left( \frac{\hbar}{2\pi i} x \frac{df}{dx} \right) = \frac{\hbar}{2\pi i} f\end{aligned}$$

$$\text{Hence } [\hat{P}_x, \hat{x}] = \frac{\hbar}{2\pi i} \hat{I}$$

where  $\hat{I}$  is the unit operator. Since  $\hat{P}_x$  and  $\hat{x}$  do not commute, the linear momentum of the particle along the x-axis and its position along the x-axis cannot be determined simultaneously.

### Commutation Rules Amongst the Components of Angular Momentum

#### Commutator of $\hat{L}_x$ and $\hat{L}_y$

We have

$$\begin{aligned}\hat{L}_x \hat{L}_y &= \left[ \frac{\hbar}{2\pi i} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \right] \left[ \frac{\hbar}{2\pi i} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \right] \\ &= -\frac{\hbar^2}{4\pi^2} \left[ y \frac{\partial}{\partial z} \left( z \frac{\partial}{\partial x} \right) - y \frac{\partial}{\partial z} \left( x \frac{\partial}{\partial z} \right) - z \frac{\partial}{\partial y} \left( z \frac{\partial}{\partial x} \right) + z \frac{\partial}{\partial y} \left( x \frac{\partial}{\partial z} \right) \right] \\ &= -\frac{\hbar^2}{4\pi^2} \left[ \left[ yz \frac{\partial^2}{\partial z \partial x} + y \frac{\partial}{\partial x} \right] - \left[ yx \frac{\partial^2}{\partial z^2} \right] - \left[ z^2 \frac{\partial^2}{\partial y \partial x} \right] + \left[ zx \frac{\partial^2}{\partial y \partial z} \right] \right]\end{aligned}$$

$$\begin{aligned}\hat{L}_y \hat{L}_x &= \left[ \frac{\hbar}{2\pi i} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \right] \left[ \frac{\hbar}{2\pi i} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \right] \\ &= -\frac{\hbar^2}{4\pi^2} \left[ z \frac{\partial}{\partial x} \left( y \frac{\partial}{\partial z} \right) - z \frac{\partial}{\partial x} \left( z \frac{\partial}{\partial y} \right) - x \frac{\partial}{\partial z} \left( y \frac{\partial}{\partial z} \right) + x \frac{\partial}{\partial z} \left( z \frac{\partial}{\partial y} \right) \right] \\ &= -\frac{\hbar^2}{4\pi^2} \left[ \left[ zy \frac{\partial^2}{\partial x \partial z} \right] - \left[ z^2 \frac{\partial^2}{\partial x \partial y} \right] - \left[ xy \frac{\partial^2}{\partial z^2} \right] + \left[ xz \frac{\partial^2}{\partial z \partial y} + x \frac{\partial}{\partial y} \right] \right]\end{aligned}$$

Hence,

$$\begin{aligned}
 [\hat{L}_x, \hat{L}_y] &= \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x \\
 &= -\frac{\hbar^2}{4\pi^2} \left( y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) \frac{\hbar^2}{4\pi^2} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \\
 &= \frac{i\hbar}{2\pi} \left[ \frac{h}{2\pi i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \right] \frac{i\hbar}{2\pi} \hat{L}_z \quad \text{(AIV.3)}
 \end{aligned}$$

**Commutator of  $\hat{L}_y$  and  $\hat{L}_z$ , and  $\hat{L}_z$  and  $\hat{L}_x$**

Proceeding similarly, it can be shown that

$$[\hat{L}_y, \hat{L}_z] = \hat{L}_y \hat{L}_z - \hat{L}_z \hat{L}_y = \frac{i\hbar}{2\pi} \hat{L}_x \quad \text{(AIV.4)}$$

$$[\hat{L}_z, \hat{L}_x] = \hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z = \frac{i\hbar}{2\pi} \hat{L}_y \quad \text{(AIV.5)}$$

**Implication of the Commutation Rules**

Since the commutators  $[\hat{L}_x, \hat{L}_y]$ ,  $[\hat{L}_y, \hat{L}_z]$  and  $[\hat{L}_z, \hat{L}_x]$  are not equal to zero, it follows that the simultaneous determination of  $L_x$  and  $L_y$ ,  $L_y$  and  $L_z$ , and  $L_z$  and  $L_x$  are not possible. This, in turn, implies that if the value of any one component (say,  $L_z$ ) is determined precisely then the other two components (say,  $L_x$  and  $L_y$ ) cannot be determined precisely at the same time.

**Commutation Rules Between the Square of Angular Momentum and the Components of Angular Momentum**

**Commutator of  $\hat{L}^2$  and  $\hat{L}_x$**

We have

$$[\hat{L}^2, \hat{L}_x] = \hat{L}^2 \hat{L}_x - \hat{L}_x \hat{L}^2$$

Since  $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ , we get

$$\begin{aligned}
 [\hat{L}^2, \hat{L}_x] &= (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) \hat{L}_x - \hat{L}_x (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) \\
 &= \hat{L}_x \hat{L}_x^2 + \hat{L}_y \hat{L}_x^2 + \hat{L}_z \hat{L}_x^2 - \hat{L}_x \hat{L}_x^2 - \hat{L}_x \hat{L}_y^2 - \hat{L}_x \hat{L}_z^2 \\
 &= (\hat{L}_x \hat{L}_x^2 - \hat{L}_x^2 \hat{L}_x) + (\hat{L}_y \hat{L}_x^2 - \hat{L}_x^2 \hat{L}_y) + (\hat{L}_z \hat{L}_x^2 - \hat{L}_x^2 \hat{L}_z) \\
 &= (\hat{L}_y \hat{L}_x - \hat{L}_x \hat{L}_y) + (\hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z) \quad \text{(AIV.6)}
 \end{aligned}$$

To evaluate each of the two terms in the right side of Eq. (AIV.6), we proceed as follows

$$\hat{L}_y \hat{L}_x - \hat{L}_x \hat{L}_y = \hat{L}_y \hat{L}_x - \hat{L}_x \hat{L}_y$$

Adding and subtracting the term  $\hat{L}_y \hat{L}_x \hat{L}_y$ , we get

$$\begin{aligned}
 \hat{L}_y^2 \hat{L}_x - \hat{L}_x \hat{L}_y^2 &= \hat{L}_y \hat{L}_y \hat{L}_x - \hat{L}_y \hat{L}_x \hat{L}_y + \hat{L}_y \hat{L}_x \hat{L}_y - \hat{L}_x \hat{L}_y \hat{L}_y \\
 &= \hat{L}_y (\hat{L}_y \hat{L}_x - \hat{L}_x \hat{L}_y) + (\hat{L}_y \hat{L}_x - \hat{L}_x \hat{L}_y) \hat{L}_y \\
 &= \hat{L}_y \left( -\frac{i\hbar}{2\pi} \hat{L}_z \right) + \left( -\frac{i\hbar}{2\pi} \hat{L}_z \right) \hat{L}_y \\
 &= -\frac{i\hbar}{2\pi} (\hat{L}_y \hat{L}_z + \hat{L}_z \hat{L}_y) \quad \text{(AIV.7)}
 \end{aligned}$$

Similarly,

$$\hat{L}_z^2 \hat{L}_x - \hat{L}_x \hat{L}_z^2 = \hat{L}_z \hat{L}_z \hat{L}_x - \hat{L}_z \hat{L}_x \hat{L}_z + (\hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z) \hat{L}_z$$

Adding and subtracting the term  $\hat{L}_z \hat{L}_x \hat{L}_z$ , we get

$$\begin{aligned}
 \hat{L}_z^2 \hat{L}_x - \hat{L}_x \hat{L}_z^2 &= \hat{L}_z \hat{L}_z \hat{L}_x - \hat{L}_z \hat{L}_x \hat{L}_z + \hat{L}_z \hat{L}_x \hat{L}_z - \hat{L}_x \hat{L}_z \hat{L}_z \\
 &= \hat{L}_z (\hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z) + (\hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z) \hat{L}_z \\
 &= \hat{L}_z \left( \frac{i\hbar}{2\pi} \hat{L}_y \right) + \left( \frac{i\hbar}{2\pi} \hat{L}_y \right) \hat{L}_z \\
 &= \frac{i\hbar}{2\pi} (\hat{L}_z \hat{L}_y + \hat{L}_y \hat{L}_z) \quad \text{(AIV.8)}
 \end{aligned}$$

Substituting Eqs (AIV.7) and (AIV.8) in Eq. (AIV.6), we get

$$[\hat{L}^2, \hat{L}_x] = \left[ -\frac{i\hbar}{2\pi} (\hat{L}_y \hat{L}_z + \hat{L}_z \hat{L}_y) \right] + \left[ \frac{i\hbar}{2\pi} (\hat{L}_z \hat{L}_y + \hat{L}_y \hat{L}_z) \right] = 0$$

Proceeding similarly, we can prove that

$$[\hat{L}^2, \hat{L}_y] = 0 \quad \text{(AIV.9)}$$

$$[\hat{L}^2, \hat{L}_z] = 0 \quad \text{(AIV.10)}$$

**Comment** Equations (AIV.9) and (AIV.10) also follow from the fact that the designation  $x$ -,  $y$ - and  $z$ -axes are matter of convenient only. All the three axes are equivalent and can be designated in any manner.)

We have the following commutation rules.

- (i) The operator  $\hat{L}^2$  commutes with each of the three components  $\hat{L}_x$ ,  $\hat{L}_y$  and  $\hat{L}_z$ .
- (ii) No two components amongst  $\hat{L}_x$ ,  $\hat{L}_y$  and  $\hat{L}_z$  commute with each other.

**Commutator of  $\hat{L}^2$  and  $\hat{L}_y$  and  $\hat{L}^2$  and  $\hat{L}_z$**

**Physical Significance of Commutation Rules**

From these rules, it follows that

The value of  $L^2$  (or  $L = \sqrt{L^2}$ ) and any one component (say,  $L_x$  or  $L_y$  or  $L_z$ ) can be defined simultaneously. By convention, the component is chosen to be  $L_z$  (i.e. component of angular momentum along  $z$ -axis, which is the direction of magnetic field). This means if  $L_z$  is chosen to be defined along with  $L^2$ , then the values of  $L_x$  and  $L_y$  cannot be defined simultaneously. This fact is in agreement with uncertainty principle. Had the values of all the three components  $L_x$ ,  $L_y$  and  $L_z$  been defined precisely, this will lead to the precise location of the axis of rotation along which the linear momentum (having zero value) is precisely known. This will violate the uncertainty principle as the precise values of linear momentum in any direction and location of this direction cannot be determined simultaneously.

## ANNEXURE V

### Transformation of Laplacian Operator from Cartesian Coordinates to Spherical Polar Coordinates

The Laplacian operator is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (\text{AV.1})$$

In Annexure III, we have derived the following expressions.

$$\begin{aligned} \frac{\partial}{\partial x} &= (\sin \theta \cos \varphi) \frac{\partial}{\partial r} + \left( \frac{\cos \theta \cos \varphi}{r} \right) \frac{\partial}{\partial \theta} + \left( -\frac{\sin \varphi}{r \sin \theta} \right) \frac{\partial}{\partial \varphi} \\ \frac{\partial}{\partial y} &= (\sin \theta \sin \varphi) \frac{\partial}{\partial r} + \left( \frac{\cos \theta \sin \varphi}{r} \right) \frac{\partial}{\partial \theta} + \left( \frac{\cos \varphi}{r \sin \theta} \right) \frac{\partial}{\partial \varphi} \\ \frac{\partial}{\partial z} &= (\cos \theta) \frac{\partial}{\partial r} + \left( -\frac{\sin \theta}{r} \right) \frac{\partial}{\partial \theta} \end{aligned}$$

We now derive the expressions of  $\partial^2/\partial x^2$ ,  $\partial^2/\partial y^2$  and  $\partial^2/\partial z^2$ .

$$\begin{aligned} \frac{\partial^2}{\partial x^2} &= \left[ \sin \theta \cos \varphi \frac{\partial}{\partial r} + \frac{\cos \theta \cos \varphi}{r} \frac{\partial}{\partial \theta} - \frac{\sin \varphi}{r \sin \theta} \frac{\partial}{\partial \varphi} \right] \\ &\quad \left[ \sin \theta \cos \varphi \frac{\partial}{\partial r} + \frac{\cos \theta \cos \varphi}{r} \frac{\partial}{\partial \theta} - \frac{\sin \varphi}{r \sin \theta} \frac{\partial}{\partial \varphi} \right] \\ &= \sin \theta \cos \varphi \left[ \sin \theta \cos \varphi \frac{\partial^2}{\partial r^2} - \frac{\cos \theta \cos \varphi}{r^2} \frac{\partial}{\partial \theta} \right. \\ &\quad \left. + \frac{\cos \theta \cos \varphi}{r} \frac{\partial^2}{\partial r \partial \theta} + \frac{\sin \varphi}{r^2 \sin \theta} \frac{\partial}{\partial \varphi} - \frac{\sin \varphi}{r \sin \theta} \frac{\partial^2}{\partial r \partial \varphi} \right] \\ &\quad + \frac{\cos \theta \cos \varphi}{r} \left[ \cos \theta \cos \varphi \frac{\partial}{\partial r} + \sin \theta \cos \varphi \frac{\partial^2}{\partial \theta \partial r} - \frac{\sin \theta \cos \varphi}{r} \frac{\partial}{\partial \theta} \right. \\ &\quad \left. + \frac{\cos \theta \cos \varphi}{r} \frac{\partial^2}{\partial \theta^2} + \frac{\sin \varphi \cos \theta}{r \sin^2 \theta} \frac{\partial}{\partial \varphi} - \frac{\sin \varphi}{r \sin \theta} \frac{\partial^2}{\partial \theta \partial \varphi} \right] \end{aligned}$$

## ANNEXURE VI Splitting of Schrödinger Equation of Hydrogen Atom

$$\begin{aligned}
& -\frac{\sin \varphi}{r \sin \theta} \left[ -\sin \theta \sin \varphi \frac{\partial}{\partial r} + \sin \theta \cos \varphi \frac{\partial}{\partial \varphi} \frac{\partial}{\partial r} - \frac{\cos \theta \sin \varphi}{r} \frac{\partial}{\partial \theta} \right. \\
& \quad \left. + \frac{\cos \theta \cos \varphi}{r} \frac{\partial^2}{\partial \varphi \partial \theta} - \frac{\cos \varphi}{r \sin \theta} \frac{\partial}{\partial \varphi} \frac{\partial}{\partial \theta} \frac{\partial^2}{\partial \varphi^2} \right] \\
& = \sin^2 \theta \cos^2 \varphi \frac{\partial^2}{\partial r^2} + \frac{\cos \theta}{r^2} \left( \sin^2 \varphi - 2 \sin \theta \cos^2 \varphi \right) \frac{\partial}{\partial \theta} \\
& \quad + \frac{2 \sin \theta \cos \theta \cos^2 \varphi}{r} \frac{\partial^2}{\partial r \partial \theta} + \frac{\sin \varphi \cos \varphi}{r^2} \left[ 1 + \frac{\cos^2 \theta}{\sin^2 \theta} + \frac{1}{\sin^2 \theta} \right] \frac{\partial}{\partial \varphi} \\
& \quad - \frac{2 \cos \varphi \sin \varphi}{r} \frac{\partial^2}{\partial r \partial \varphi} + \frac{1}{r} (\cos^2 \theta \cos^2 \varphi + \sin^2 \varphi) \frac{\partial}{\partial \theta} \\
& \quad - \frac{2 \cos \theta \cos \varphi \sin \varphi}{r^2 \sin \theta} \frac{\partial^2}{\partial \theta \partial \varphi} + \frac{\cos^2 \theta \cos^2 \varphi}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{\sin^2 \varphi}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}
\end{aligned}$$

Similarly, we can proceed to show that

$$\begin{aligned}
\frac{\partial^2}{\partial y^2} & = \sin^2 \theta \sin^2 \varphi \frac{\partial^2}{\partial r^2} + \frac{\cos \theta}{r^2} \left[ \frac{\cos^2 \varphi}{\sin \theta} - 2 \sin \theta \sin^2 \varphi \right] \frac{\partial}{\partial \theta} \\
& \quad + \frac{2 \cos \theta \sin \theta \sin^2 \varphi}{r} \frac{\partial^2}{\partial r \partial \theta} - \frac{\sin \varphi \cos^2 \varphi}{r^2} \left[ 1 + \frac{\cos^2 \theta}{\sin^2 \theta} + \frac{1}{\sin^2 \theta} \right] \frac{\partial}{\partial \varphi} \\
& \quad + \frac{2 \cos \varphi \sin \varphi}{r} \frac{\partial^2}{\partial r \partial \varphi} + \frac{1}{r} (\cos^2 \varphi + \sin^2 \varphi \cos^2 \theta) \frac{\partial}{\partial \theta} \\
& \quad + \frac{2 \cos \theta \cos \varphi \sin \varphi}{r^2 \sin \theta} \frac{\partial^2}{\partial \theta \partial \varphi} + \frac{\cos^2 \theta \sin^2 \varphi}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{\cos^2 \varphi}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \\
\frac{\partial^2}{\partial z^2} & = \cos^2 \theta \frac{\partial^2}{\partial r^2} + \frac{2 \sin \theta \cos \theta}{r^2} \frac{\partial}{\partial \theta} - \frac{2 \cos \theta \sin \theta}{r} \frac{\partial^2}{\partial r \partial \theta} \\
& \quad + \frac{\sin^2 \theta}{r} \frac{\partial}{\partial r} + \frac{\sin^2 \theta}{r^2} \frac{\partial^2}{\partial \theta^2}
\end{aligned}$$

With these derivatives, Eq. (AV.1) becomes

$$\begin{aligned}
\nabla^2 & = \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \left( \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \\
& = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}
\end{aligned}$$

The Schrödinger equation for hydrogen atom can be split into two equations representing respectively the motion of centre of mass of atom and the motion of electron relative to the nucleus within the atom.

The coordinates of centre of mass is

$$x_c = \frac{m_n x_n + m_e x_e}{m_n + m_e}; \quad y_c = \frac{m_n y_n + m_e y_e}{m_n + m_e}; \quad z_c = \frac{m_n z_n + m_e z_e}{m_n + m_e} \quad (\text{AVI.1})$$

To describe the motion of electron relative to nucleus, we define internal coordinates as

$$x = x_n - x_e; \quad y = y_n - y_e; \quad z = z_n - z_e \quad (\text{AVI.2})$$

By chain rule, we write

$$\begin{aligned}
\frac{\partial}{\partial x_n} & = \frac{\partial x_c}{\partial x_n} \frac{\partial}{\partial x_c} + \frac{\partial x}{\partial x_n} \frac{\partial}{\partial x} \\
\frac{\partial^2}{\partial x_n^2} & = \left( \frac{\partial}{\partial x_n} \right) \left( \frac{\partial}{\partial x_n} \right) = \left[ \frac{\partial x_c}{\partial x_n} \frac{\partial}{\partial x_c} + \frac{\partial x}{\partial x_n} \frac{\partial}{\partial x} \right] \left[ \frac{\partial x_c}{\partial x_n} \frac{\partial}{\partial x_c} + \frac{\partial x}{\partial x_n} \frac{\partial}{\partial x} \right] \\
& = \left( \frac{\partial x_c}{\partial x_n} \right)^2 \frac{\partial^2}{\partial x_c^2} + \left( \frac{\partial x}{\partial x_n} \right)^2 \frac{\partial^2}{\partial x^2} + 2 \left( \frac{\partial x_c}{\partial x_n} \right) \left( \frac{\partial x}{\partial x_n} \right) \frac{\partial^2}{\partial x_c \partial x}
\end{aligned} \quad (\text{AVI.3})$$

Now from Eqs (AVI.1) and (AVI.2), we get

$$\frac{\partial x_c}{\partial x_n} = \frac{m_n}{m_n + m_e} \quad \text{and} \quad \frac{\partial x}{\partial x_n} = 1$$

With these, Eq. (AVI.3) becomes

$$\frac{\partial^2}{\partial x_n^2} = \left( \frac{m_n}{m_n + m_e} \right)^2 \frac{\partial^2}{\partial x_c^2} + \frac{\partial^2}{\partial x^2} + \frac{2 m_n}{m_n + m_e} \frac{\partial^2}{\partial x_c \partial x} \quad (\text{AVI.4})$$

Similar expressions for  $y_n$  and  $z_n$  components are

$$\frac{\partial^2}{\partial y_n^2} = \left( \frac{m_n}{m_n + m_e} \right)^2 \frac{\partial^2}{\partial y_c^2} + \frac{\partial^2}{\partial y^2} + \frac{2 m_n}{m_n + m_e} \frac{\partial^2}{\partial y_c \partial y} \quad (\text{AVI.5})$$

$$\frac{\partial^2}{\partial z_n^2} = \left( \frac{m_n}{m_n + m_e} \right)^2 \frac{\partial^2}{\partial z_c^2} + \frac{\partial^2}{\partial z^2} + \frac{2 m_n}{m_n + m_e} \frac{\partial^2}{\partial z_c \partial z} \quad (\text{AVI.6})$$

Similarly, we have

$$\frac{\partial}{\partial x_e} = \frac{\partial x_e}{\partial x_e} \frac{\partial}{\partial x_e} + \frac{\partial x}{\partial x_e} \frac{\partial}{\partial x}$$

$$\frac{\partial^2}{\partial x_e^2} = \left( \frac{\partial}{\partial x_e} \right) \left( \frac{\partial}{\partial x_e} \right) = \left[ \frac{\partial x_e}{\partial x_e} \frac{\partial}{\partial x_e} + \frac{\partial x}{\partial x_e} \frac{\partial}{\partial x} \right] \left[ \frac{\partial x_e}{\partial x_e} \frac{\partial}{\partial x_e} + \frac{\partial x}{\partial x_e} \frac{\partial}{\partial x} \right]$$

$$= \left( \frac{\partial x_e}{\partial x_e} \right)^2 \frac{\partial^2}{\partial x_e^2} + \left( \frac{\partial x}{\partial x_e} \right) \frac{\partial^2}{\partial x^2} + 2 \left( \frac{\partial x_e}{\partial x_e} \right) \left( \frac{\partial x}{\partial x_e} \right) \frac{\partial^2}{\partial x_e \partial x} \quad (\text{AVL.7})$$

From Eqs (AVL.1) and (AVL.2), we get

$$\left( \frac{\partial x_e}{\partial x_e} \right) = \frac{m_e}{m_n + m_e} \quad \text{and} \quad \frac{\partial x}{\partial x_e} = -1$$

With these, Eq. (AVL.7) becomes

$$\frac{\partial^2}{\partial x_e^2} = \left( \frac{m_e}{m_n + m_e} \right)^2 \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial x^2} - \frac{2m_e}{m_n + m_e} \frac{\partial^2}{\partial x_e \partial x} \quad (\text{AVL.8})$$

Similar expressions for  $y_e$  and  $z_e$  components are

$$\frac{\partial^2}{\partial y_e^2} = \left( \frac{m_e}{m_n + m_e} \right)^2 \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial y^2} - \frac{2m_e}{m_n + m_e} \frac{\partial^2}{\partial y_e \partial y} \quad (\text{AVL.9})$$

$$\frac{\partial^2}{\partial z_e^2} = \left( \frac{m_e}{m_n + m_e} \right)^2 \frac{\partial^2}{\partial z_e^2} + \frac{\partial^2}{\partial z^2} - \frac{2m_e}{m_n + m_e} \frac{\partial^2}{\partial z_e \partial z} \quad (\text{AVL.10})$$

The Schrödinger equations for hydrogen atom is

$$\left[ -\frac{h^2}{8\pi^2 m_e} \left( \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right) - \frac{h^2}{8\pi^2 m_n} \left( \frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2} + \frac{\partial^2}{\partial z_n^2} \right) - \frac{Ze^2}{(4\pi\epsilon_0)r} \right] \psi_{\text{total}} = E_{\text{total}} \psi_{\text{total}}$$

Substituting Eqs (AVL.4) to (AVL.6) and Eqs (AVL.8) to (AVL.10), we get

$$\left[ -\frac{h^2}{8\pi^2 (m_n + m_e)} \left( \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right) - \frac{h^2}{8\pi^2} \left( \frac{1}{m_e} + \frac{1}{m_n} \right) \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{(4\pi\epsilon_0)r} \right] \psi_{\text{total}} = E_{\text{total}} \psi_{\text{total}} \quad (\text{AVL.11})$$

If the distance  $r$  between electron and nucleus is expressed in the relative coordinates,

we see that the operator in Eq. (AVL.11) consists of two terms, each depending on the two sets of independent coordinates. Hence, we can write

$$\psi_{\text{total}} = \psi_e \psi_n \quad (\text{AVL.12})$$

where  $\psi_e$  describes the motion of centre of mass of hydrogen atom and  $\psi_n$  describes the motion of electron relative to the nucleus within the atom. Substituting Eq. (AVL.12) in Eq. (AVL.11), we get

$$\begin{aligned} & -\frac{h^2}{8\pi^2 (m_n + m_e)} \psi_e \left( \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right) \psi_n \\ & - \frac{h^2}{8\pi^2} \left( \frac{1}{m_e} + \frac{1}{m_n} \right) \psi_e \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_n \\ & - \frac{Ze^2}{(4\pi\epsilon_0)r} \psi_e \psi_n = E_{\text{total}} \psi_e \psi_n \end{aligned}$$

Dividing throughout by  $\psi_e \psi_n$ , we get

$$\begin{aligned} & -\frac{h^2}{8\pi^2 (m_n + m_e)} \frac{1}{\psi_e} \left( \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right) \psi_e \\ & - \frac{h^2}{8\pi^2} \left( \frac{1}{m_e} + \frac{1}{m_n} \right) \frac{1}{\psi_n} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_n \\ & - \frac{Ze^2}{(4\pi\epsilon_0)r} = E_{\text{total}} \end{aligned} \quad (\text{AVL.13})$$

The first term of the above expression depends only on the coordinates  $x_e, y_e$  and  $z_e$  and the second and third terms taken together on the coordinates  $x, y$  and  $z$ , and the sum of these two terms is a constant. This is possible if each term is separately constant. Writing

$$E_{\text{total}} = E_{\text{trans}} + E_{\text{elec}} \quad (\text{AVL.14})$$

we can write

$$-\frac{h^2}{8\pi^2 (m_n + m_e)} \left( \frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2} \right) \psi_e = E_{\text{trans}} \psi_e \quad (\text{AVL.15})$$

and

$$\left[ -\frac{h^2}{8\pi^2 \mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{(4\pi\epsilon_0)r} \right] \psi_n = E_{\text{elec}} \psi_n \quad (\text{AVL.16})$$

where  $\frac{1}{m_e} + \frac{1}{m_n}$  has been replaced by  $1/\mu$ , where  $\mu$  is the reduced mass of electron.



## ANNEXURE VII Atomic Units

In the calculations of atomic and molecular quantities, the system of atomic units is widely used. In this system, the electronic mass ( $m_e$ ), the electronic charge ( $e$ ), the basic unit of angular momentum ( $\hbar/2\pi$ ) and the permittivity ( $4\pi\epsilon_0$ ) are assigned a value of unity. Thus

$$m_e = 1, \quad e = 1, \quad \hbar/2\pi = 1 \quad \text{and} \quad 4\pi\epsilon_0 = 1$$

All other physical quantities can be expressed in terms of the atomic units. The following derived atomic units are also used.

1. *Length* The length is expressed in the atomic unit of length known as a *Bohr*. This is equal to the first Bohr radius. Thus

$$a_0 = \frac{(\hbar/2\pi)^2}{m_e(e/\sqrt{4\pi\epsilon_0})^2} = 1$$

2. *Energy* The energy is expressed in the atomic unit of energy known as a *hartree*. This is twice of the ionization energy of atomic hydrogen. Thus

$$E_0 = \frac{m_e(e/\sqrt{4\pi\epsilon_0})^4}{(\hbar/2\pi)^2} = \frac{(e/\sqrt{4\pi\epsilon_0})^2}{a_0} = 1$$

3. *Time* The time is expressed in the atomic unit of time which is the period of rotation of an electron in the first Bohr orbit, i.e.

$$t_0 = \frac{(\hbar/2\pi)^3}{m_e(e/\sqrt{4\pi\epsilon_0})^4} = 1$$

4. *Speed* The speed is expressed in the atomic unit of speed which is the speed of an electron in the first Bohr orbit, i.e.

$$c_0 = \frac{(e/\sqrt{4\pi\epsilon_0})^2}{(\hbar/2\pi)} = 1$$

5. *Electric potential* This is expressed in atomic unit of potential which corresponds to the potential energy of 1 C of charge in the first Bohr orbit, i.e.

$$V_0 = \frac{\text{Potential energy of an electron in the first Bohr orbit}}{\text{Electronic charge}} = \frac{(e/\sqrt{4\pi\epsilon_0})^2/a_0}{e} = \frac{e}{(4\pi\epsilon_0)a_0} = 1$$

6. *Magnetic dipole moment* This is expressed in the atomic unit of magnetic dipole moment which is twice of the Bohr magneton, i.e.

$$p_0 = 2\mu_B = \frac{e(\hbar/2\pi)}{m_e} = 1$$

Table AVII.1 records the values of atomic units in terms of SI equivalents.

The Hamiltonian operator when written in terms of atomic units becomes independent of any physical constants. For example, the Hamiltonian operator

$$H_{op} = -\frac{(\hbar/2\pi)^2}{2m_e} \nabla_1^2 - \frac{(\hbar/2\pi)^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{(4\pi\epsilon_0)r_1} - \frac{Ze^2}{(4\pi\epsilon_0)r_2} + \frac{e^2}{(4\pi\epsilon_0)r_{12}}$$

for the helium atom is simplified to

$$H_{op} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

Table AVII.1 Values of Atomic Units in SI Units

Atomic unit	SI equivalent
$m_e = 1$	$9.109\,1 \times 10^{-31} \text{ kg}$
$e = 1$	$1.602\,1 \times 10^{-19} \text{ C}$
$\hbar/2\pi = 1$	$1.054\,5 \times 10^{-34} \text{ J s}$
$4\pi\epsilon_0 = 1$	$1.112\,6 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$
$a_0 = 1 \text{ bohr}$	$5.291\,67 \times 10^{-11} \text{ m}$
$E_0 = 1 \text{ hartree}$	$4.359\,44 \times 10^{-18} \text{ J}$
$t_0 = 1$	$2.418\,89 \times 10^{-17} \text{ s}$
$c_0 = 1$	$2.187\,64 \times 10^6 \text{ m s}^{-1}$
$V_0 = 1$	$27.211 \text{ V}$
$p_0 = 1$	$1.854\,64 \times 10^{-22} \text{ J T}^{-1}$

## ANNEXURE VIII The Ladder-Operator Method Applied to Angular Momentum

The ladder-operator method can be used to determine the eigenvalues of square and z-component of angular momentum arising due to orbital or spin motion of a particle. We use symbol  $M$  instead of  $L$  to indicate that we may deal with either type of angular momentum.

### Definition of the Ladder-Operators

The ladder-operators are defined by the expressions

$$\hat{M}_+ = \hat{M}_x + i\hat{M}_y \quad \text{and} \quad \hat{M}_- = \hat{M}_x - i\hat{M}_y \quad (\text{AVIII.1})$$

Naming  $\hat{M}_+$  and  $\hat{M}_-$  as the ladder-operators will be described shortly. These are also named as the raising operator and the lowering operator, respectively.

### Expressions of $\hat{M}_+$ and $\hat{M}_-$

We have

$$\begin{aligned} \hat{M}_+ \hat{M}_- &= (\hat{M}_x + i\hat{M}_y)(\hat{M}_x - i\hat{M}_y) \\ &= \hat{M}_x^2 - i\hat{M}_x \hat{M}_y + i\hat{M}_y \hat{M}_x + \hat{M}_y^2 \\ &= (\hat{M}_x^2 - \hat{M}_y^2) - i(\hat{M}_x \hat{M}_y - \hat{M}_y \hat{M}_x) \\ &= (\hat{M}^2 - \hat{M}_z^2) - i\left(\frac{i\hbar}{2\pi} \hat{M}_z\right) \\ &= \hat{M}^2 - \hat{M}_z^2 + \frac{\hbar}{2\pi} \hat{M}_z \end{aligned} \quad (\text{AVIII.2a})$$

Similarly, it can be worked out that

$$\hat{M}_- \hat{M}_+ = \hat{M}^2 - \hat{M}_z^2 - \frac{\hbar}{2\pi} \hat{M}_z \quad (\text{AVIII.2b})$$

We have

$$\begin{aligned} [\hat{M}_+, \hat{M}_z] &= \hat{M}_+ \hat{M}_z - \hat{M}_z \hat{M}_+ \\ &= (\hat{M}_x + i\hat{M}_y) \hat{M}_z - \hat{M}_z (\hat{M}_x + i\hat{M}_y) \\ &= \hat{M}_x \hat{M}_z + i\hat{M}_y \hat{M}_z - \hat{M}_z \hat{M}_x - i\hat{M}_z \hat{M}_y \\ &= (\hat{M}_x \hat{M}_z - \hat{M}_z \hat{M}_x) + i(\hat{M}_y \hat{M}_z - \hat{M}_z \hat{M}_y) \\ &= -\frac{i\hbar}{2\pi} \hat{M}_y + i\left(\frac{i\hbar}{2\pi} \hat{M}_x\right) \\ &= -\frac{\hbar}{2\pi} (\hat{M}_x + i\hat{M}_y) = -\frac{\hbar}{2\pi} \hat{M}_+ \end{aligned} \quad (\text{AVIII.3a})$$

Similarly, it can be worked out that

$$[\hat{M}_-, \hat{M}_z] = \hat{M}_- \hat{M}_z - \hat{M}_z \hat{M}_- = \frac{\hbar}{2\pi} \hat{M}_- \quad (\text{AVIII.3b})$$

### Commutators of $\hat{M}_+$ and $\hat{M}_-$ with $\hat{M}^2$

We have

$$\begin{aligned} [\hat{M}_+, \hat{M}^2] &= \hat{M}_+ \hat{M}^2 - \hat{M}^2 \hat{M}_+ \\ &= (\hat{M}_x + i\hat{M}_y) \hat{M}^2 - \hat{M}^2 (\hat{M}_x + i\hat{M}_y) \\ &= \hat{M}_x \hat{M}^2 + i\hat{M}_y \hat{M}^2 - \hat{M}^2 \hat{M}_x - i\hat{M}^2 \hat{M}_y \\ &= (\hat{M}_x \hat{M}^2 - \hat{M}^2 \hat{M}_x) + i(\hat{M}_y \hat{M}^2 - \hat{M}^2 \hat{M}_y) \\ &= [\hat{M}_x, \hat{M}^2] + i[\hat{M}_y, \hat{M}^2] \\ &= 0 + i(0) = 0 \end{aligned} \quad (\text{AVIII.4a})$$

Similarly, it can be worked out that

$$[\hat{M}_-, \hat{M}^2] = 0 \quad (\text{AVIII.4b})$$

Since  $\hat{M}^2$  and  $\hat{M}_z$  commute with each other, they will have the common set of eigenfunctions. We may write the eigenvalue expressions as

$$\hat{M}^2 Y = cY \quad (\text{AVIII.5})$$

$$\hat{M}_z^2 Y = cY \quad (\text{AVIII.6})$$

Operating  $\hat{M}_+$  on Eq. (AVIII.6), we get

$$\hat{M}_+ (\hat{M}^2 Y) = \hat{M}_+ (cY)$$

Since  $\hat{M}_+$  and  $\hat{M}^2$  commute with each other, we write the above expression as

$$\hat{M}^2 (\hat{M}_+ Y) = c (\hat{M}_+ Y) \quad (\text{AVIII.7})$$

that is, the function  $\hat{M}_+ Y$  is also an eigenfunction of  $\hat{M}^2$  with the same eigenvalue as that of the function  $Y$ .

Operating  $\hat{M}_+$  on Eq. (AVIII.7) would give

$$\hat{M}_+ [\hat{M}^2 (\hat{M}_+ Y)] = \hat{M}_+ [c (\hat{M}_+ Y)]$$

$$\text{or} \quad (\hat{M}_+ \hat{M}^2) (\hat{M}_+ Y) = c \hat{M}_+ (\hat{M}_+ Y) \quad \text{or} \quad (\hat{M}^2 \hat{M}_+) (\hat{M}_+ Y) = c \hat{M}_+^2 Y$$

$$\text{or} \quad \hat{M}^2 (\hat{M}_+^2 Y) = c (\hat{M}_+^2 Y)$$

that is, the function  $\hat{M}_+^2 Y$  is also an eigenfunction of  $\hat{M}^2$  with the same eigenvalue  $c$ .

The successive application of  $\hat{M}_+$  on Eq. (AVIII.6) would give

$$\hat{M}^2 (\hat{M}_+^k Y) = c (\hat{M}_+^k Y) \quad (\text{AVIII.8a})$$

Similarly, it can be worked out that

$$\hat{M}^2 (\hat{M}_-^k Y) = c (\hat{M}_-^k Y) \quad (\text{AVIII.8b})$$

Equations (AVIII.8a) and (AVIII.8b) may be written together as

$$\hat{M}^2 (\hat{M}_\pm^k Y) = c (\hat{M}_\pm^k Y) \quad (\text{AVIII.9})$$

Operating  $\hat{M}_+$  on Eq. (AVIII.5), we get

$$\hat{M}_+ (\hat{M}^2 Y) = \hat{M}_+ (cY) \quad (\text{AVIII.10})$$

### Successive Operations of $\hat{M}_+$ and $\hat{M}_-$ on Eq. (AVIII.5)

From Eq. (AVIII.3a), we get

$$[\hat{M}_+, \hat{M}_z] = \hat{M}_+ \hat{M}_z - \hat{M}_z \hat{M}_+ = -\frac{h}{2\pi} \hat{M}_+ \quad (\text{AVIII.11})$$

i.e.

$$\hat{M}_+ \hat{M}_z = \hat{M}_z \hat{M}_+ - \frac{h}{2\pi} \hat{M}_+$$

With this, Eq. (AVIII.10) becomes

$$\left( \hat{M}_z \hat{M}_+ - \frac{h}{2\pi} \hat{M}_+ \right) Y = \hat{M}_+ (bY) \quad (\text{AVIII.12})$$

or  $\hat{M}_z (\hat{M}_+ Y) = (b + h/2\pi) (\hat{M}_+ Y)$

that is, the function  $\hat{M}_+ Y$  is an eigenfunction of  $\hat{M}_z$  with eigenvalue  $b + h/2\pi$ . In other words, operating on the eigenfunction  $Y$  with the raising operator  $\hat{M}_+$  converts the function  $Y$  into  $\hat{M}_+ Y$  with the eigenvalue  $h/2\pi$  higher than the eigenvalue of  $Y$ . It is for this reason, the operator  $\hat{M}_+$  is known as the raising operator.

Operating  $\hat{M}_+$  on Eq. (AVIII.12), we get

$$\hat{M}_+ [\hat{M}_z (\hat{M}_+ Y)] = \hat{M}_+ [(b + h/2\pi) (\hat{M}_+ Y)]$$

which on using Eq. (AVIII.11) becomes

$$\left( \hat{M}_z \hat{M}_+ - \frac{h}{2\pi} \hat{M}_+ \right) (\hat{M}_+ Y) = (b + h/2\pi) (\hat{M}_+^2 Y)$$

$$\text{or } \hat{M}_z (\hat{M}_+^2 Y) = \left( b + 2 \frac{h}{2\pi} \right) (\hat{M}_+^2 Y)$$

that is, the successive operation of  $\hat{M}_+$  on Eq. (AVIII.5) raises each time the eigenvalue by  $h/2\pi$ . Thus, we can write

$$\hat{M}_z (\hat{M}_+^k Y) = \left( b + k \frac{h}{2\pi} \right) (\hat{M}_+^k Y) \quad (\text{AVIII.13a})$$

Similarly, we can work out that

$$\hat{M}_z (\hat{M}_-^k Y) = \left( b - k \frac{h}{2\pi} \right) (\hat{M}_-^k Y) \quad (\text{AVIII.13b})$$

Equations (AVIII.13a) and (AVIII.13b) may be written together as

$$\hat{M}_z (\hat{M}_\pm^k Y) = \left( b \pm k \frac{h}{2\pi} \right) (\hat{M}_\pm^k Y) \quad (\text{AVIII.14})$$

Equation (AVIII.14) displays that the eigenvalues of  $\hat{M}_z$  are spaced at intervals of  $h/2\pi$ .

We have

$$\hat{M}^2 (\hat{M}_\pm Y) = c (\hat{M}_\pm Y) \quad (\text{Eq. AVIII.9})$$

$$\hat{M}_z (\hat{M}_\pm^k Y) = \left( b \pm k \frac{h}{2\pi} \right) (\hat{M}_\pm^k Y) \quad (\text{Eq. AVIII.14})$$

**Relation Between the Constants  $b$  and  $c$**

Operating  $\hat{M}_z$  on Eq. (AVIII.14), we get

$$\begin{aligned} \hat{M}_z [\hat{M}_z (\hat{M}_\pm^k Y)] &= \hat{M}_z \left[ \left( b \pm k \frac{h}{2\pi} \right) (\hat{M}_\pm^k Y) \right] \\ &= \left( b \pm k \frac{h}{2\pi} \right) [\hat{M}_z (\hat{M}_\pm^k Y)] \\ &= \left( b \pm k \frac{h}{2\pi} \right)^2 (\hat{M}_\pm^k Y) \end{aligned}$$

(AVIII.15)

Since  $\hat{M}^2 = \hat{M}_x^2 + \hat{M}_y^2 + \hat{M}_z^2$ , we can write Eq. (AVIII.9) as

$$(\hat{M}_x^2 + \hat{M}_y^2) (\hat{M}_\pm^k Y) + \hat{M}_z^2 (\hat{M}_\pm^k Y) = c (\hat{M}_\pm^k Y)$$

which on using Eq. (AVIII.15) becomes

$$(\hat{M}_x^2 + \hat{M}_y^2) (\hat{M}_\pm^k Y) = \left[ c - \left( b \pm k \frac{h}{2\pi} \right)^2 \right] (\hat{M}_\pm^k Y)$$

The operators  $\hat{M}_x$  and  $\hat{M}_y$  correspond to non-negative physical quantities and hence will have non-negative eigenvalues. Hence, we will have

$$c - \left( b \pm k \frac{h}{2\pi} \right)^2 \geq 0 \quad (\text{AVIII.16})$$

In Eq. (AVIII.16), the first term remains constant while the second term increases with increase in the value of  $k$ . In order that Eq. (AVIII.16) holds good, the value of  $k$  will have upper bounds. Let these be represented as  $k'$  and  $k''$  for plus and minus combinations, respectively. The corresponding functions may be written as

$$Y_{\max} = \hat{M}_-^{k'} Y \quad \text{and} \quad Y_{\min} = \hat{M}_-^{k''} Y$$

$$\text{with } \hat{M}_z Y_{\max} = \left( b + k' \frac{h}{2\pi} \right) Y_{\max} \quad \text{and} \quad \hat{M}_z Y_{\min} = \left( b - k'' \frac{h}{2\pi} \right) Y_{\min}.$$

For a value of  $k$  greater than  $k'$  or  $k''$ , Eq. (AVIII.16) is not satisfied. This fact is accounted for by writing

$$\hat{M}_+ Y_{\max} = 0 \quad \text{and} \quad \hat{M}_- Y_{\min} = 0 \quad (\text{AVIII.17})$$

Operating  $\hat{M}_-$  on  $\hat{M}_+ Y_{\max}$ , we get

$$\hat{M}_- (\hat{M}_+ Y_{\max}) = 0$$

which on using Eq. (AVIII.2b) becomes

$$\left( \hat{M}^2 - \hat{M}_z^2 - \frac{h}{2\pi} \hat{M}_z \right) Y_{\max} = 0$$

$$\text{This gives } c - b_{\max}^2 - \frac{h}{2\pi} b_{\max} = 0. \quad (\text{AVIII.19a})$$

Similarly operating  $\hat{M}_+ Y_{\min}$  by  $\hat{M}_+$  and then using Eq. (AVIII.2a), we get

$$c - b_{\min}^2 + \frac{h}{2\pi} b_{\min} = 0 \quad (\text{AVIII.19b})$$

### Upper Bounds of the Values of $b$

Eliminating  $c$  in Eqs (AVIII.19a) and (AVIII.19b), we get

$$b_{\max}^2 + \frac{h}{2\pi} b_{\max} = b_{\min}^2 - \frac{h}{2\pi} b_{\min}$$

This expression will be satisfied only when

$$b_{\max} = -b_{\min} \quad \text{i.e.} \quad b + k' \left( \frac{h}{2\pi} \right) = - \left[ b - k'' \left( \frac{h}{2\pi} \right) \right]$$

$$\text{or} \quad b = \left( \frac{k'' - k'}{2} \right) \left( \frac{h}{2\pi} \right) \quad (\text{AVIII.20})$$

The expressions of  $b_{\max}$  and  $b_{\min}$  become

$$\begin{aligned} b_{\max} &= b + k' \left( \frac{h}{2\pi} \right) = \left( \frac{k'' - k'}{2} \right) \left( \frac{h}{2\pi} \right) + k' \left( \frac{h}{2\pi} \right) \\ &= \left( \frac{k'' + k'}{2} \right) \left( \frac{h}{2\pi} \right) \quad (\text{AVIII.21}) \\ b_{\min} &= -b_{\max} = - \left( \frac{k'' + k'}{2} \right) \left( \frac{h}{2\pi} \right) \quad (\text{AVIII.22}) \end{aligned}$$

The expression of  $c$  is

$$\begin{aligned} c &= b_{\max}^2 + \left( \frac{h}{2\pi} \right) b_{\max} = \left( \frac{k'' + k'}{2} \cdot \frac{h}{2\pi} \right)^2 + \left( \frac{h}{2\pi} \right) \left( \frac{k'' + k'}{2} \cdot \frac{h}{2\pi} \right) \\ &= \left( \frac{k'' + k'}{2} \right) \left( \frac{k'' + k'}{2} + 1 \right) \left( \frac{h}{2\pi} \right)^2 \quad (\text{AVIII.23}) \end{aligned}$$

Writing  $(k'' + k')/2$  by  $l$ , we get

$$\begin{aligned} b_{\max} &= l(h/2\pi) \quad \text{and} \quad b_{\min} = -l(h/2\pi) \quad (\text{AVIII.24}) \\ c &= l(l+1)(h/2\pi)^2 \quad (\text{AVIII.25}) \end{aligned}$$

Since  $b$  changes in a step of  $h/2\pi$  (Eq. AVIII.14), we cover the entire range from  $b_{\min}$  to  $b_{\max}$  by writing the expression

$$b = m(h/2\pi) \quad (\text{AVIII.26})$$

where  $m$  varies from  $-l$  to  $+l$  with a stepwise increase of one, i.e.

$$-l, -(l-1), \dots, (l-1), l \quad (\text{AVIII.27})$$

The value of  $l$  may be integral or half-integral depending upon the even or odd value of  $k'' + k'$ .

**Case 1  $l$  has integral values** In this case,  $k' = k''$  and thus  $b = 0$ . (Eq. AVIII.20)

Moreover,  $l = \frac{k' + k''}{2} = \text{integral value}$

For this case, we have

$$\widehat{M}_z(\widehat{M}_\pm^m Y) = \left[ m \left( \frac{h}{2\pi} \right) \right] (\widehat{M}_\pm^m Y); \quad m = 0, \pm 1, \pm 2, \dots, \pm l$$

$$\widehat{M}_z^2(\widehat{M}_\pm^l Y) = l(l+1) \left( \frac{h}{2\pi} \right)^2 (\widehat{M}_\pm^l Y); \quad l = 0, 1, 2, \dots$$

**Case 2  $l$  has half-integral values** For a case where  $k'' = k' + 1$ ,  $b = (1/2)(h/2\pi)$  and the value of  $l$  will be

$$l = \frac{k' + k''}{2} = \frac{k' + k' + 1}{2} = k' + \frac{1}{2} = \text{half-integral values.}$$

For this case, we have

$$\widehat{M}_z(\widehat{M}_\pm^m Y) = \left[ m \left( \frac{h}{2\pi} \right) \right] (\widehat{M}_\pm^m Y); \quad m = \pm \frac{1}{2}, \pm \frac{3}{2}, \dots, \pm l$$

$$\widehat{M}_z^2(\widehat{M}_\pm^l Y) = l(l+1) \left( \frac{h}{2\pi} \right)^2 (\widehat{M}_\pm^l Y); \quad l = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$$

The function  $Y$  depends on two numbers  $l$  and  $m$  and is written as  $Y_{l,m}$  such that

$$\widehat{M}_z^2 Y_{l,m} = l(l+1) \left( \frac{h}{2\pi} \right)^2 Y_{l,m} \quad (\text{AVIII.28})$$

$$\widehat{M}_z Y_{l,m} = m \left( \frac{h}{2\pi} \right) Y_{l,m} \quad (\text{AVIII.29})$$

The subscript  $l$  and  $m$  in  $Y_{l,m}$  characterise the eigenvalues of  $\widehat{M}^2$  and  $\widehat{M}_z$ , respectively.

As stated above, the value of  $m$  varies from  $-l$  to  $+l$  with a stepwise increase of one.

Since the  $z$ -component of angular momentum for the function  $\widehat{M}_+ Y_{l,m}$  is  $h/2\pi$  higher than that of the function  $Y_{l,m}$ , we may write the function  $\widehat{M}_+ Y_{l,m}$  as

$$\widehat{M}_+ Y_{l,m} = K_+ Y_{l,m+1} \quad (\text{AVIII.30})$$

where  $K_+$  is a suitable multiplier. Similarly, we may write

$$\widehat{M}_- Y_{l,m} = K_- Y_{l,m-1} \quad (\text{AVIII.31})$$

**Evaluation of Multiplier  $K_+$**  Multiplying each side of Eq. (AVIII.30) by its complex conjugate followed by integration, we get

$$\int (\widehat{M}_+ Y_{l,m})^* (\widehat{M}_+ Y_{l,m}) d\tau = K_+^2 \int Y_{l,m+1}^* Y_{l,m+1} d\tau \quad (\text{AVIII.32}^\dagger)$$

Assuming the function  $Y_{l,m}$ 's to constitute orthonormal set, we get

$$\begin{aligned} K_+^2 &= \int (\widehat{M}_+ Y_{l,m})^* (\widehat{M}_+ Y_{l,m}) d\tau = \int (\widehat{M}_x + i\widehat{M}_y) Y_{l,m} d\tau \\ &= \int (\widehat{M}_x Y_{l,m})^* \widehat{M}_x Y_{l,m} d\tau + i \int (\widehat{M}_x Y_{l,m})^* \widehat{M}_y Y_{l,m} d\tau \quad (\text{AVIII.33}) \end{aligned}$$

<sup>†</sup> We assume that the multiplier  $K_+$  has a real value.

### Explicit Form of the Functions $Y$

#### Expressions

Relating  $Y_{l,m}$  with  $Y_{l,m+1}$  and  $Y_{l,m-1}$

Using the Hermitian property of  $\widehat{M}_x$  and  $\widehat{M}_y$ , Eq. (AVIII.33) can be written as

$$\begin{aligned} K_+^2 &= \int Y_{l,m} \widehat{M}_x^* (\widehat{M}_x Y_{l,m})^* d\tau + i \int Y_{l,m} \widehat{M}_y^* (\widehat{M}_y Y_{l,m})^* d\tau \\ &= \int Y_{l,m} (\widehat{M}_x^* + i \widehat{M}_y^*) (\widehat{M}_x Y_{l,m})^* d\tau \\ &= \int Y_{l,m} (\widehat{M}_x^* + i \widehat{M}_y^*) (\widehat{M}_x - i \widehat{M}_y) Y_{l,m}^* d\tau \end{aligned}$$

Taking the complex conjugate of the above expression, we get

$$\begin{aligned} K_+^2 &= \int Y_{l,m}^* (\widehat{M}_x - i \widehat{M}_y) (\widehat{M}_x + i \widehat{M}_y) Y_{l,m} d\tau \\ &= \int Y_{l,m}^* \left[ \widehat{M}_x^2 + \widehat{M}_y^2 + i (\widehat{M}_x \widehat{M}_y - \widehat{M}_y \widehat{M}_x) \right] Y_{l,m} d\tau \\ &= \int Y_{l,m}^* \left[ \widehat{M}^2 - \widehat{M}_z^2 + i \left( \frac{i\hbar}{2\pi} \widehat{M}_z \right) \right] Y_{l,m} d\tau \\ &= \left[ l(l+1) \left( \frac{\hbar}{2\pi} \right)^2 - m^2 \left( \frac{\hbar}{2\pi} \right)^2 - \left( \frac{\hbar}{2\pi} \right) m \left( \frac{\hbar}{2\pi} \right) \right] \int Y_{l,m}^* Y_{l,m} d\tau \\ &= [l(l+1) - m^2 - m] \left( \frac{\hbar}{2\pi} \right)^2 = [l^2 - m^2 + l - m] \left( \frac{\hbar}{2\pi} \right)^2 \end{aligned}$$

$$\text{i.e. } K_+ = \sqrt{l(l-m)(l+m+1)} \left( \frac{\hbar}{2\pi} \right) \quad (\text{AVIII.34})$$

**Evaluation of Multiplier  $K_-$**  Proceeding similarly, it can be worked out that

$$K_- = \sqrt{l(l+m)(l-m+1)} \left( \frac{\hbar}{2\pi} \right) \quad (\text{AVIII.35})$$

The function  $Y_{l,l}$  can be determined by using the expression

$$M_+ Y_{l,l} = 0 \quad (\text{AVIII.36})$$

**Expression of  $M_+$**  The operator  $\widehat{M}_+$  is

$$\begin{aligned} \widehat{M}_+ &= \widehat{M}_x + i \widehat{M}_y \\ &= -\frac{\hbar}{2\pi i} \left( \sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \\ &\quad + i \frac{\hbar}{2\pi i} \left( \cos \varphi \frac{\partial}{\partial \theta} - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \end{aligned}$$

$$\begin{aligned} &= \frac{\hbar}{2\pi} \left[ (\cos \varphi + i \sin \varphi) \frac{\partial}{\partial \theta} + i \cot \theta (\cos \varphi + i \sin \varphi) \frac{\partial}{\partial \varphi} \right] \\ &= \left( \frac{\hbar}{2\pi} \right) (e^{i\varphi}) \left( \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) \end{aligned} \quad (\text{AVIII.37})$$

Since the operator  $\widehat{M}_+$  involves  $\theta$  and  $\varphi$  variables, we write the function  $Y$  as

$$Y_{l,m} = \Theta_\theta \Phi_\varphi \quad (\text{AVIII.38})$$

**Form of the Function  $\Phi_\varphi$**  The form of the function  $\Phi_\varphi$  may be determined by using the expression

$$\widehat{M}_z Y_{l,m} = m \left( \frac{\hbar}{2\pi} \right) Y_{l,m} \quad (\text{Eq. AVIII.29})$$

Since  $\widehat{M}_z = (\hbar/2\pi i) \partial/\partial \varphi$ , we have

$$\frac{\hbar}{2\pi i} \frac{\partial}{\partial \varphi} \Theta_\theta \Phi_\varphi = m \left( \frac{\hbar}{2\pi} \right) \Theta_\theta \Phi_\varphi$$

$$\text{or } \frac{\hbar}{2\pi i} \Theta_\theta \frac{d}{d\varphi} \Phi_\varphi = m \left( \frac{\hbar}{2\pi} \right) \Theta_\theta \Phi_\varphi$$

Cancelling  $(\hbar/2\pi) \Theta_\theta$ , we get

$$\frac{d\Phi}{d\varphi} = im\Phi \quad \text{or} \quad \frac{d\Phi}{\Phi} = im d\varphi$$

$$\text{or } \ln \Phi = im\varphi + \text{constant} \quad \text{or} \quad \Phi = Ae^{im\varphi} \quad (\text{AVIII.39})$$

From the boundary condition  $\Phi_\varphi = \Phi_{\varphi+2\pi}$ , we get

$$Ae^{im\varphi} = Ae^{im(\varphi+2\pi)} \quad \text{or} \quad 1 = e^{2\pi im}$$

$$\text{or } \cos(2\pi m) + i \sin(2\pi m) = 1$$

This will hold good if  $m = 0, \pm 1, \pm 2, \dots$

The constant  $A$  is determined by the normalization of the function  $\Phi$ , i.e.

$$\int_0^{2\pi} \Phi^* \Phi d\varphi = 1$$

This gives

$$A^2 \int_0^{2\pi} e^{-im\varphi} e^{im\varphi} d\varphi = 1$$

$$\text{or } A^2 \int_0^{2\pi} d\varphi = 1 \quad \text{or } A^2(2\pi) = 1 \quad \text{or } A = 1/\sqrt{2\pi}$$

Hence, the function  $\Phi$  is

$$\Phi_m = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \quad ; \quad m = 0, \pm 1, \pm 2, \dots \quad (\text{AVIII.40})$$

With this, the function  $Y_{l,m}$  becomes

$$Y_{l,m} = \Theta_{\theta} \left( \frac{1}{\sqrt{2\pi}} e^{im\varphi} \right) \quad (\text{AVIII.41})$$

**Form of the Function  $\Theta_{\theta}$**  Substituting Eqs (AVIII.37) and (AVIII.41) in Eq. (AVIII.36), we get

$$\left( \frac{h}{2\pi} \right) e^{i\varphi} \left( \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) \left( \frac{1}{\sqrt{2\pi}} \Theta_{\theta} e^{im\varphi} \right) = 0$$

$$\text{or } \left( \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) \Theta_{\theta} e^{im\varphi} = 0$$

$$\text{or } e^{im\varphi} \frac{d}{d\theta} \Theta_{\theta} + i \cot \theta \Theta_{\theta} \frac{d}{d\varphi} e^{im\varphi} = 0$$

$$\text{or } e^{im\varphi} \frac{d}{d\theta} \Theta_{\theta} + i \cot \theta \Theta_{\theta} (i m e^{im\varphi}) = 0$$

This gives

$$\frac{d}{d\theta} \Theta - l (\cot \theta) \Theta = 0$$

$$\text{or } \frac{d\Theta}{\Theta} = l \cot \theta \, d\theta = l \frac{\cos \theta}{\sin \theta} \, d\theta = l \frac{d(\sin \theta)}{\sin \theta}$$

which on integration gives

$$\ln \Theta = l \ln (\sin \theta) + \text{constant}$$

$$\text{or } \Theta = N \sin^l \theta \quad (\text{AVIII.42})$$

The constant  $N$  is determined via the normalization of the function  $\Theta$  by using the expression

$$\int_0^{\pi} \Theta^* \Theta \sin \theta \, d\theta = 1 \quad (\text{AVIII.43})$$

Substituting the expression of  $\Theta$  and carrying out the integration<sup>†</sup>, we get

$$N = \left[ \frac{(2l+1)!^{1/2}}{2} \right] \frac{1}{2^l l!} \quad (\text{AVIII.44})$$

With this, the function  $\Theta_l$  becomes

$$\Theta_{l,l} = \left[ \frac{(2l+1)!^{1/2}}{2} \right] \frac{1}{2^l l!} \sin^l \theta \quad (\text{AVIII.45})$$

The function  $Y_{l,l}$  becomes

$$Y_{l,l} = \Theta_{l,l} \Phi_l = \left[ \frac{(2l+1)!^{1/2}}{2} \right] \frac{1}{2^l l!} \sin^l \theta \left( \frac{1}{\sqrt{2\pi}} e^{il\varphi} \right) \quad (\text{AVIII.46})$$

Using the lowering operator  $\hat{M}_-$  on the function  $Y_{l,m}$ , we get

$$\hat{M}_- Y_{l,m} = \sqrt{(l+m)(l-m+1)} \left( \frac{h}{2\pi} \right) Y_{l,m-1}$$

For  $m = l$ , we get

$$\hat{M}_- Y_{l,l} = \sqrt{2l} \left( \frac{h}{2\pi} \right) Y_{l,l-1} \quad (\text{AVIII.47})$$

The operator  $\hat{M}_-$  is

$$\begin{aligned} \hat{M}_- &= \hat{M}_x - i \hat{M}_y \\ &= \left( -\frac{h}{2\pi i} \right) \left( \sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \\ &\quad - i \frac{h}{2\pi i} \left( \cos \varphi \frac{\partial}{\partial \theta} - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \end{aligned}$$

$$\frac{1}{N^2} = \int_0^{\pi} \Theta^2 \sin \theta \, d\theta = \int_0^{\pi} \sin^{2l+1} \theta \, d\theta = \int_0^{\pi} \sin^{2l} \theta \, d(-\cos \theta)$$

$$= \sin^{2l} \theta (-\cos \theta) \Big|_0^{\pi} - \int_0^{\pi} d(\sin^{2l} \theta) (-\cos \theta) = 0 + \int_0^{\pi} 2l \sin^{2l-1} \theta \cos^2 \theta \, d\theta$$

$$= (2l) \left[ \int_0^{\pi} \sin^{2l-1} \theta \, d\theta - \int_0^{\pi} \sin^{2l+1} \theta \, d\theta \right] = \left( \frac{2l}{2l+1} \right) \int_0^{\pi} \sin^{2l-1} \theta \, d\theta$$

$$= \left( \frac{2l}{2l+1} \right) \left( \frac{2l-2}{2l-1} \right) \dots \frac{2}{3} (-\cos \theta) \Big|_0^{\pi} = \frac{(2^l)(l-1)(l-2) \dots 1}{(2l+1)(2l-1) \dots 3} \quad (2)$$

$$= \frac{(2)^{2^l} l!}{(2l+1)(2l-1) \dots 3} \frac{(2l)(2l-2) \dots 2}{(2l)(2l-2) \dots 2} = \frac{(2)(2^l l!)}{(2l+1)!}$$

$$\text{Hence } N = \left[ \frac{(2l+1)!^{1/2}}{2} \right] \frac{1}{2^l l!}$$

$$= \left( -\frac{h}{2\pi} \right) \left[ (\cos \varphi - i \sin \varphi) \frac{\partial}{\partial \theta} - i \cot \theta (\cos \varphi - i \sin \varphi) \frac{\partial}{\partial \varphi} \right]$$

$$= \left( -\frac{h}{2\pi} \right) (e^{-i\varphi}) \left( \frac{\partial}{\partial \theta} - i \cot \theta \frac{\partial}{\partial \varphi} \right) \quad (\text{AVIII.48})$$

$$\text{Hence } \widehat{M}_- Y_{l,l} = \left[ \left( -\frac{h}{2\pi} \right) (e^{-i\varphi}) \left( \frac{\partial}{\partial \theta} - i \cot \theta \frac{\partial}{\partial \varphi} \right) \right] \left[ (N \sin^l \theta) \left( \frac{1}{\sqrt{2\pi}} e^{il\varphi} \right) \right]$$

$$= N \left( \frac{1}{\sqrt{2\pi}} \right) \left( -\frac{h}{2\pi} \right) (e^{-i\varphi}) [l \sin^{l-1} \theta \cos \theta - i(l) \cot \theta \sin^l \theta]$$

$$= \left( -\frac{h}{2\pi} \right) \left( \frac{1}{\sqrt{2\pi}} e^{i(l-1)\varphi} \right) (2N \sin^{l-1} \theta \cos \theta) \quad (\text{AVIII.49})$$

Substituting Eq. (AVIII.49) in Eq. (AVIII.47), we get

$$\left( -\frac{h}{2\pi} \right) \left( \frac{1}{\sqrt{2\pi}} e^{i(l-1)\varphi} \right) (2N \sin^{l-1} \theta \cos \theta) = \sqrt{2l} \left( \frac{h}{2\pi} \right) Y_{l,l-1}$$

This gives  $Y_{l,l-1} = \Theta_{l,l-1} \Phi_{l-1}$

where  $\Theta_{l,l-1} = -N\sqrt{2l} \sin^{l-1} \theta \cos \theta$  (AVIII.50)

$$\Phi_{l-1} = \frac{1}{\sqrt{2\pi}} e^{i(l-1)\varphi} \quad (\text{AVIII.51})$$

Substituting the expression of  $N$  from Eq. (AVIII.44) into Eq. (AVIII.50), we get

$$\Theta_{l,l-1} = - \left[ \frac{(2l+1)!^{1/2}}{2} \right] \frac{1}{2^l l!} \sqrt{2l} \sin^{l-1} \theta \cos \theta$$

$$= - \left[ \frac{l(2l+1)!^{1/2}}{2^l l!} \right] \frac{1}{2^l l!} \sin^{l-1} \theta \cos \theta \quad (\text{AVIII.52})$$

**Expression for the Function  $Y_{l,l-2}$**

Using the expression

$$\widehat{M}_- Y_{l,m} = \sqrt{(l+m)(l-m+1)} \left( \frac{h}{2\pi} \right) Y_{l,m-1} \quad (\text{AVIII.53})$$

For  $m = l-1$ , we get

$$\widehat{M}_- Y_{l,l-1} = \sqrt{(2l-1)2} \left( \frac{h}{2\pi} \right) Y_{l,l-2} \quad (\text{AVIII.54})$$

$$\text{Now } \widehat{M}_- Y_{l,l-1} = \left( -\frac{h}{2\pi} \right) (e^{-i\varphi}) \left( \frac{\partial}{\partial \theta} - i \cot \theta \frac{\partial}{\partial \varphi} \right)$$

$$\times \left[ \left( -N\sqrt{2l} \sin^{l-1} \theta \cos \theta \right) \left( \frac{1}{\sqrt{2\pi}} e^{i(l-1)\varphi} \right) \right]$$

$$= N\sqrt{2l} \left( \frac{h}{2\pi} \right) (e^{-i\varphi}) \left[ \frac{1}{\sqrt{2\pi}} \right] \left[ e^{i(l-1)\varphi} \frac{d}{d\theta} (\sin^{l-1} \theta \cos \theta) \right]$$

$$- i \cot \theta \sin^{l-1} \theta \cos \theta \frac{d}{d\varphi} (e^{i(l-1)\varphi})$$

$$= (N)\sqrt{2l} \left( \frac{h}{2\pi} \right) (e^{-i\varphi}) \left( \frac{1}{\sqrt{2\pi}} e^{i(l-1)\varphi} \right) [(l-1) \sin^{l-2} \theta \cos^2 \theta$$

$$+ (\sin^{l-1} \theta)(-\sin \theta) - i \cot \theta \sin^{l-1} \theta \cos \theta \{i(l-1)\}]$$

$$= (N)\sqrt{2l} \left( \frac{h}{2\pi} \right) (e^{-i\varphi}) \left( \frac{1}{\sqrt{2\pi}} e^{i(l-1)\varphi} \right) [2(l-1) \sin^{l-2} \theta \cos^2 \theta - \sin^l \theta]$$

$$= (N)\sqrt{2l} \left( \frac{h}{2\pi} \right) \left( \frac{1}{\sqrt{2\pi}} e^{i(l-2)\varphi} \right) [\sin^{l-2} \theta (2l-1) \cos^2 \theta - 1]$$

Substituting the above expression in Eq. (AVIII.54), we get

$$Y_{l,l-2} = \Theta_{l,l-2} \Phi_{l-2}$$

where

$$\Theta_{l,l-2} = N \left( \frac{l}{2l-1} \right)^{1/2} [\sin^{l-2} \theta \{(2l-1) \cos^2 \theta - 1\}] \quad (\text{AVIII.55})$$

$$\Phi_{l-2} = \frac{1}{\sqrt{2\pi}} e^{i(l-2)\varphi} \quad (\text{AVIII.56})$$

Substituting the expression of  $N$  in Eq. (AVIII.55), we get

$$\Theta_{l,l-2} = \left[ \frac{(2l+1)!^{1/2}}{2} \right] \frac{1}{2^l l!} \left( \frac{l}{2l-1} \right)^{1/2} [\sin^{l-2} \theta \{(2l-1) \cos^2 \theta - 1\}]$$

$$= \left[ \frac{l(2l+1)!^{1/2}}{2(2l-1)} \right] \frac{1}{2^{l+1}} [\sin^{l-2} \theta \{(2l-1) \cos^2 \theta - 1\}] \quad (\text{AVIII.57})$$

## ANNEXURE IX Electronic Transitions in Hydrogen Atom including Spin-Orbit Coupling

The electronic states along with their term symbols of hydrogen atom (see, Section 1.13) are as follows.

Configuration	Term symbol
1s, 2s, 3s, ...	$^2S_{1/2}$
2p, 3p, 4p, ...	$^2P_{1/2}, ^2P_{3/2}$
3d, 4d, 5d, ...	$^2D_{3/2}, ^2D_{5/2}$
4f, 5f, ...	$^2F_{5/2}, ^2F_{7/2}$

According to Hund's rule (see, Section 1.14), the relative energies of states follow the order:

$$\begin{aligned} n=2 & \quad ^2P_{1/2} < ^2S_{1/2} < ^2P_{3/2} \\ n=3 & \quad ^2P_{1/2} < ^2S_{1/2} < ^2D_{3/2} \approx ^2P_{3/2} < ^2D_{5/2} \\ n=4 & \quad ^2P_{1/2} < ^2S_{1/2} < ^2D_{3/2} \approx ^2P_{3/2} < ^2F_{5/2} \approx ^2D_{5/2} < ^2F_{7/2} \end{aligned}$$

While discussing electronic spectrum of hydrogen atom including spin-orbit coupling, the selection rules to be followed are

$$\Delta L = \pm 1 \quad \text{and} \quad \Delta J = 0, \pm 1$$

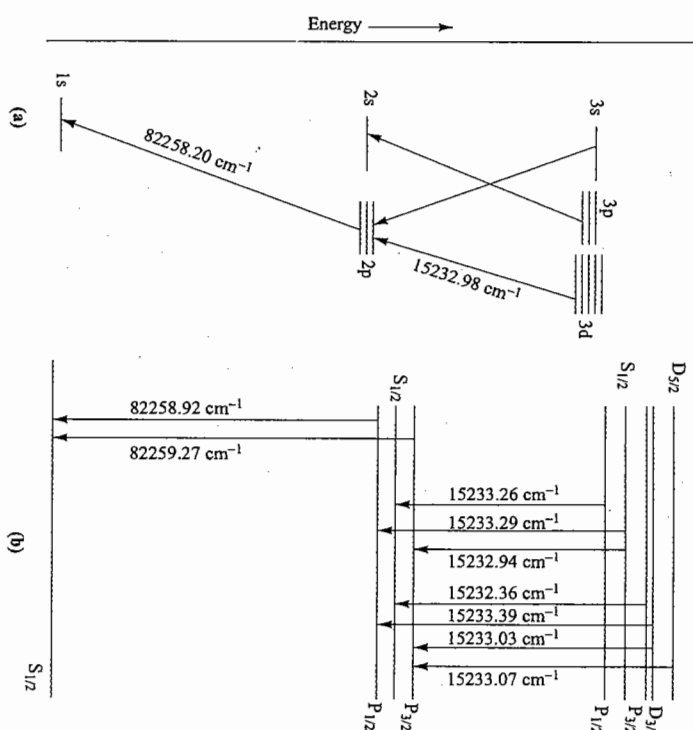
Some of the allowed electronic transitions in hydrogen atom are as follows.

$$\begin{aligned} ^2S_{1/2}(1s) & \leftarrow ^2P_{1/2}(2p) & ^2P_{1/2}(2p) & \leftarrow ^2S_{1/2}(3s) \\ ^2S_{1/2}(1s) & \leftarrow ^2P_{3/2}(2p) & ^2P_{3/2}(3p) & \leftarrow ^2S_{1/2}(3s) \\ ^2S_{1/2}(2s) & \leftarrow ^2P_{1/2}(3p) & ^2P_{3/2}(2p) & \leftarrow ^2D_{3/2}(3d) \\ ^2S_{1/2}(2s) & \leftarrow ^2P_{3/2}(3p) & ^2P_{3/2}(2p) & \leftarrow ^2D_{5/2}(3d) \end{aligned}$$

These transitions are shown in Fig. AIX.1. In the absence of spin-orbit coupling five spectral series (Lyman, Balmer, Paschen, Brackett and Pfund) are observed. In the presence of spin-orbit coupling, each absorption is found to be more than one absorption (observable under high resolution).

The states  $S_{1/2}$  and  $P_{1/2}$  are two-fold degenerate corresponding to  $m_j = +1/2$  and  $-1/2$ . The states  $P_{3/2}$  and  $D_{3/2}$  are four-fold degenerate corresponding to  $m_j = +3/2, +1/2, -1/2$  and  $-3/2$ . The state  $D_{5/2}$  is six-fold degenerate corresponding to  $m_j = +5/2, +3/2, +1/2, -1/2, -3/2$  and  $-5/2$ . These degeneracy are lifted up in the presence of magnetic field.

Fig. AIX.1 Hydrogen spectrum (a) with no spin-orbit coupling, and (b) with spin-orbit coupling.





## ANNEXURE X First-Order Perturbation Theory

### The Method of Perturbation

The electronic Hamiltonian operator for the helium atom is

$$H_{\text{op}} = \left( -\frac{\hbar^2}{8\pi^2 m} \nabla_1^2 - \frac{Ze^2}{(4\pi\epsilon_0)r_1} \right) + \left( -\frac{\hbar^2}{8\pi^2 m} \nabla_2^2 - \frac{Ze^2}{(4\pi\epsilon_0)r_2} \right) + \frac{e^2}{(4\pi\epsilon_0)r_{12}} \quad (\text{AX.1})$$

$$= \hat{H}_1^{(0)} + \hat{H}_2^{(0)} + \hat{H}' = \hat{H}^{(0)} + \hat{H}'$$

where  $\hat{H}^{(0)}$  is the unperturbed operator (which is sum of the operators  $\hat{H}_1^{(0)}$  and  $\hat{H}_2^{(0)}$  for electrons 1 and 2, respectively), and  $\hat{H}'$  is the perturbation in the operator  $H_{\text{op}}$ . The Schrödinger equation

$$H_{\text{op}} \psi = E\psi \quad (\text{AX.2})$$

is not exactly solvable. However, if the perturbation is ignored, the problem is solvable since we can write

$$H_{\text{op}}^{(0)} \psi^{(0)} = E^{(0)} \psi^{(0)} \quad (\text{AX.3})$$

$$\text{where } H_{\text{op}}^{(0)} = \hat{H}_1^{(0)} + \hat{H}_2^{(0)} \quad (\text{AX.4})$$

$$\psi^{(0)} = \psi_1^{(0)} \psi_2^{(0)} \quad (\text{AX.5})$$

The solution of Eq. (AX.3) goes as follows.

$$\begin{aligned} H_{\text{op}}^{(0)} \psi^{(0)} &= (\hat{H}_1^{(0)} + \hat{H}_2^{(0)}) (\psi_1^{(0)} \psi_2^{(0)}) \\ &= \psi_2^{(0)} (\hat{H}_1^{(0)} \psi_1^{(0)}) + \psi_1^{(0)} (\hat{H}_2^{(0)} \psi_2^{(0)}) \\ &= \psi_2^{(0)} (E_1^{(0)} \psi_1^{(0)}) + \psi_1^{(0)} (E_2^{(0)} \psi_2^{(0)}) \\ &= (E_1^{(0)} + E_2^{(0)}) (\psi_1^{(0)} \psi_2^{(0)}) \end{aligned} \quad (\text{AX.6})$$

that is, the energy of the system is sum of the energies of the two electrons.

The approximate solution of Eq. (AX.2) can be carried out by the perturbation method. The Schrödinger equation for the perturbed system may be written as

$$(\hat{H}^{(0)} + \lambda \hat{H}') \psi_n = E_n \psi_n \quad (\text{AX.7})$$

where  $\lambda$  is some parameter which may be identified with the extent of perturbation (for  $\lambda = 0$ , the perturbed system is reduced to unperturbed system with  $\psi_n$  reducing to  $\psi_n^{(0)}$  and for  $\lambda = 1$ , the problem is under full perturbation). The wave function  $\psi_n$  besides depending upon the electronic coordinates will also depend on the parameter  $\lambda$ . Similarly, the energy  $E_n$  will depend on the parameter  $\lambda$ . The wave function  $\psi_n$  and energy  $E_n$  may be expanded as Taylor series in power of  $\lambda$ .

$$\begin{aligned} \psi_n &= \psi_n|_{\lambda=0} + \frac{\partial \psi_n}{\partial \lambda} \bigg|_{\lambda=0} \lambda + \frac{\partial^2 \psi_n}{\partial \lambda^2} \bigg|_{\lambda=0} \lambda^2 + \dots \\ &= \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots \end{aligned} \quad (\text{AX.8})$$

$$\begin{aligned} E_n &= E_n|_{\lambda=0} + \frac{dE_n}{d\lambda} \bigg|_{\lambda=0} \lambda + \frac{d^2 E_n}{d\lambda^2} \bigg|_{\lambda=0} \lambda^2 + \dots \\ &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \end{aligned} \quad (\text{AX.9})$$

The term containing  $\lambda$  is known as the first-order perturbation, the term containing  $\lambda^2$  as the second-order perturbation and so on. Substitution of Eq. (AX.8) and Eq. (AX.9) in Eq. (AX.7), we get

$$\begin{aligned} (\hat{H}^{(0)} + \lambda \hat{H}') (\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots) \\ = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) (\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots) \end{aligned}$$

This can be expressed as

$$\begin{aligned} \hat{H}^{(0)} \psi_n^{(0)} + \lambda (\hat{H}^{(0)} \psi_n^{(1)} + \hat{H}' \psi_n^{(0)} + \lambda^2 \hat{H}^{(0)} \psi_n^{(2)} + \lambda \hat{H}' \psi_n^{(1)} + \dots) \\ = E_n^{(0)} \psi_n^{(0)} + \lambda (E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)} + \lambda^2 (E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + \dots) \end{aligned}$$

The above expression holds good for any value of  $\lambda$ . Equating the coefficients of  $\lambda$ 's on either sides of the above expression, we get

$$\hat{H}^{(0)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}; \quad (\text{Zero-order perturbation equation})$$

$$\hat{H}' \psi_n^{(0)} + \hat{H}^{(0)} \psi_n^{(1)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \psi_n^{(1)}; \quad (\text{First-order perturbation equation})$$

$$\hat{H}^{(0)} \psi_n^{(2)} + \hat{H}' \psi_n^{(1)} = E_n^{(2)} \psi_n^{(0)} + E_n^{(1)} \psi_n^{(1)}; \quad (\text{Second-order perturbation equation})$$

and so on.

### Correction due to the First-order Perturbation

Considering the first-order perturbation equation, we have

$$\begin{aligned} \hat{H}' \psi_n^{(0)} + \hat{H}^{(0)} \psi_n^{(1)} \\ = (\hat{H}^{(0)} - E_n^{(0)}) \psi_n^{(1)} = (\hat{H}' - \hat{H}) \psi_n^{(0)} \end{aligned} \quad (\text{AX.10})$$

$$= E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \psi_n^{(1)} \quad (\text{AX.11})$$

The function  $\psi_n^{(1)}$  can be written in terms of a complete set of unperturbed wave functions as

$$\psi_n^{(1)} = \sum_j a_j \psi_j^{(0)} \quad (\text{AX.11})$$

Substituting Eq. (AX.11) in Eq. (AX.10), we get

$$(\hat{H}^{(0)} - E_n^{(0)}) \left( \sum_j a_j \psi_j^{(0)} \right) = (\hat{H}' - \hat{H}) \psi_n^{(0)}$$

Multiplying the above expression by  $\psi_m^{(0)*}$  and integrating over the configuration space, we get

$$\int \psi_m^{(0)*} (\hat{H}^{(0)} - E_n^{(0)}) \left( \sum_j a_j \psi_j^{(0)} \right) d\tau = \int \psi_m^{(0)*} (\hat{H}' - \hat{H}) \psi_n^{(0)} d\tau$$

$$\text{i.e. } \sum_j a_j (E_j^{(0)} - E_n^{(0)}) \int \psi_m^{(0)*} \psi_j^{(0)} d\tau = E_n^{(1)} \int \psi_m^{(0)*} \psi_n^{(0)} d\tau - \int \psi_m^{(0)*} \hat{H}' \psi_n^{(0)} d\tau$$

$$\text{i.e. } \sum_j a_j (E_j^{(0)} - E_n^{(0)}) \delta_{mj} = E_n^{(1)} \delta_{mn} - \int \psi_m^{(0)*} \hat{H}' \psi_n^{(0)} d\tau$$

where  $\delta_{mj}$  is Kronecker delta ( $\delta = 1$  for  $m = j$  and  $\delta = 0$  for  $m \neq j$ ). The above expression is equivalent to

$$a_m (E_m^{(0)} - E_n^{(0)}) = E_n^{(1)} \delta_{mn} - \int \psi_m^{(0)*} \hat{H}' \psi_n^{(0)} d\tau \quad (\text{AX.12})$$

For  $m = n$ , we get

$$0 = E_n^{(1)} - \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} d\tau$$

that is

$$E_n^{(1)} = \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} d\tau \quad (\text{AX.13})$$

Equation (AX.13) states that the first-order correction in energy is obtainable from the unperturbed wave function  $\psi_n^{(0)}$  and the perturbed part of the Hamiltonian.

The coefficient  $a_m$  with  $m \neq n$  in the perturbed wave function (Eq. AX.11) as obtained from Eq. (AX.12) is given by

$$a_m = \frac{\int \psi_m^{(0)*} \hat{H}' \psi_n^{(0)} d\tau}{E_n^{(0)} - E_m^{(0)}} = \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \quad (\text{AX.14})$$

provided  $E_n^{(0)} \neq E_m^{(0)}$ . This amounts to the fact that the states to which the corrections are being carried out must be nondegenerate. The coefficient  $a_n$  may be determined by normalizing the perturbed wave function  $\psi_n$  ( $= \psi_n^{(0)} + \psi_n^{(1)}$ ). The convention is to set  $a_n = 0$  as the choice of  $a_n$  does not affect the energy correction.

$$\text{Hence } \psi_n = \psi_n^{(0)} + \sum_{m \neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} \quad (\text{AX.15})$$

### APPLICATION TO A HELIUM ATOM

For helium atom in the ground state, both the electrons are allocated to 1s orbital, for which, we have

$$\psi_{1s} = R_{1,0} \Theta_{0,0} \Phi_0 = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \cdot \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2\pi}} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$$

$$\text{Hence } \psi^{(0)} = \psi_1^{(0)} \psi_2^{(0)} = \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 e^{-2Zr/a_0} e^{-2Zr/a_0} \quad (\text{AX.16})$$

The energy of an electron in the orbitals of hydrogen-like species is

$$E_n = -\frac{Z^2}{n^2} \left[ \frac{e^2}{2(4\pi\epsilon_0)a_0} \right] = -\frac{Z^2}{n^2} (13.6 \text{ eV})$$

$$\text{Hence } E^{(0)} = E_1^{(0)} + E_2^{(0)} = 2 E_{1s}^{(0)}$$

$$= -2 \left[ \frac{2^2}{1^2} (13.6 \text{ eV}) \right] = -108.8 \text{ eV} \quad (\text{AX.17})$$

The perturbation energy is given by

$$E^{(1)} = \langle \psi^{(0)} | H' | \psi^{(0)} \rangle$$

$$\begin{aligned} &= \left\langle \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 e^{-2Zr/a_0} e^{-2Zr/a_0} \left| \frac{e^2}{(4\pi\epsilon_0)r_{12}} \right| \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 e^{-2Zr/a_0} e^{-2Zr/a_0} \right\rangle \\ &= \frac{1}{\pi^2} \left( \frac{Z}{a_0} \right)^6 \left( \frac{e^2}{4\pi\epsilon_0} \right) \left\langle e^{-2Zr/a_0} e^{-2Zr/a_0} \left| \frac{1}{r_{12}} \right| e^{-2Zr/a_0} e^{-2Zr/a_0} \right\rangle \end{aligned} \quad (\text{AX.18})$$

The element of configuration space in the above integral is

$$d\tau = dr_1 dr_2 = (r_1^2 dr_1 \sin\theta_1 d\phi_1) (r_2^2 dr_2 \sin\theta_2 d\phi_2)$$

To evaluate integral in Eq. (AX.18), we make use of the expansion  $1/r_{12}$  in terms of spherical harmonics, which we write without deriving this expression.

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \left( \frac{r'_<}{r'_>} \right) \left[ Y_l^m(\theta_1, \phi_1) \right]^* \left[ Y_l^m(\theta_2, \phi_2) \right] \quad (\text{AX.19})$$

where  $r'_<$  and  $r'_>$  are smaller and larger of  $r_1$  and  $r_2$ , respectively. Using the fact  $Y_0^0 = 1/\sqrt{4\pi}$ , we write the above expression as

$$\begin{aligned} \frac{1}{r_{12}} &= (16\pi^2) \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{2l+1} \left( \frac{r'_<}{r'_>} \right) \left[ Y_l^m(\theta_1, \phi_1) \right]^* Y_0^0(\theta_1, \phi_1) \\ &\quad \times [Y_0^0(\theta_2, \phi_2)]^* Y_l^m(\theta_2, \phi_2) \end{aligned}$$

Substitution of this expression in Eq. (AX.18), we get

$$\begin{aligned} E^{(1)} &= (16) \left( \frac{Z}{a_0} \right)^6 \left( \frac{e^2}{4\pi\epsilon_0} \right) \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{2l+1} \\ &\quad \times \int_0^{\infty} \int_0^{\infty} e^{-2Zr_1/a_0} e^{-2Zr_2/a_0} \left( \frac{r'_<}{r'_>} \right) r_1^2 dr_1 r_2^2 dr_2 \\ &\quad \times \int_0^{2\pi} \int_0^{2\pi} [Y_l^m(\theta_1, \phi_1)]^* Y_0^0(\theta_1, \phi_1) \sin\theta_1 d\theta_1 d\phi_1 \\ &\quad \times \int_0^{2\pi} \int_0^{2\pi} [Y_0^0(\theta_2, \phi_2)]^* Y_l^m(\theta_2, \phi_2) \sin\theta_2 d\theta_2 d\phi_2 \quad (\text{AX.20}) \end{aligned}$$

Since the spherical harmonics constitute an orthogonal set, each of the two integrals involving spherical harmonics will survive only for  $l = 0$  and  $m = 0$  for which each integral will be equal to unity.

Hence, Eq. (AX. 20) is reduced to

$$E^{(1)} = (16) \left( \frac{Z}{a_0} \right)^6 \left( \frac{e^2}{4\pi\epsilon_0} \right) \int_0^\infty \int_0^\infty e^{-2Zr_1/a_0} e^{-2Zr_2/a_0} \frac{1}{r_1^2} r_1^2 dr_1 r_2^2 dr_2 \quad (\text{AX. 21})$$

If we integrate first over  $r_1$ , then in the range  $0 \leq r_1 \leq r_2$ , we substitute  $r_1 = r_2$  in the range  $r_2 \leq r_1 \leq \infty$ , we substitute  $r_1 = r_1$ . Also, let us write  $2Z/a_0 = b$ . Thus

$$E^{(1)} = (16) \left( \frac{Z}{a_0} \right)^6 \left( \frac{e^2}{4\pi\epsilon_0} \right) \left[ \int_0^\infty \int_0^{r_2} e^{-br_2} \frac{r_1^2}{r_2} dr_1 + \int_{r_2}^\infty \int_{r_2}^{r_1} e^{-br_1} \frac{r_1^2}{r_1} dr_1 r_2^2 dr_2 \right] \quad (\text{AX. 22})$$

$$\text{where } I = \int_0^\infty \int_0^{r_2} e^{-br_2} \int_0^{r_2} e^{-br_1} r_1^2 dr_1 r_2^2 dr_2 \quad (\text{AX. 23})$$

$$II = \int_0^\infty \int_{r_2}^\infty e^{-br_1} \int_{r_2}^{r_1} e^{-br_1} r_1^2 dr_1 r_2^2 dr_2 \quad (\text{AX. 24})$$

Carrying out the integration within the brackets by parts, we get

$$\int_0^{r_2} r_1^2 e^{-br_1} dr_1 = \left[ \frac{r_1^2}{(-b)} - \frac{2r_1}{(-b)^2} + \frac{2}{(-b)^3} \right] e^{-br_1} \Big|_0^{r_2} = \left[ \frac{r_2^2}{(-b)} - \frac{2r_2}{(-b)^2} + \frac{2}{(-b)^3} \right] e^{-br_2} - \frac{2}{(-b)^3} \quad (\text{AX. 25})$$

$$\int_{r_2}^\infty r_1 e^{-br_1} dr_1 = \left[ \frac{r_1}{(-b)} - \frac{1}{(-b)^2} \right] e^{-br_1} \Big|_{r_2}^\infty = \left[ -\frac{r_2}{(-b)} + \frac{1}{(-b)^2} \right] e^{-br_2} \quad (\text{AX. 26})$$

$$\text{Hence, } I = \int_0^\infty \left[ \left( \frac{r_2^3}{(-b)} - \frac{2r_2^2}{(-b)^2} + \frac{2r_2}{(-b)^3} \right) e^{-2br_2} - \frac{2r_2}{(-b)^3} e^{-br_2} \right] dr_2 \quad (\text{AX. 27})$$

$$II = \int_0^\infty \left[ -\frac{r_2^2}{(-b)} + \frac{r_2}{(-b)^2} \right] e^{-2br_2} dr_2$$

Now using the standard integral

$$\int_0^\infty r^n e^{-ar} dr = \frac{n!}{a^{n+1}}$$

we get

$$I = \frac{1}{(-b)} \frac{3!}{(2b)^4} - \frac{2}{(-b)^2} \frac{2!}{(2b)^3} + \frac{2}{(-b)^3} \frac{1}{(2b)^2} - \frac{2}{(-b)^3} \frac{1}{b^2} = -\frac{6}{16b^5} - \frac{4}{8b^5} - \frac{2}{4b^5} + \frac{2}{b^5} = \frac{10}{16b^5} = \frac{5}{8b^5} \quad (\text{AX. 28})$$

$$II = -\frac{1}{(-b)} \frac{3!}{(2b)^4} + \frac{1}{(-b)^2} \frac{2!}{(2b)^3} = \frac{6}{16b^5} + \frac{2}{8b^5} = \frac{10}{16b^5} = \frac{5}{8b^5} \quad (\text{AX. 29})$$

Since  $b = 2Z/a_0$ , we get

$$I + II = \frac{5}{8b^5} + \frac{5}{8b^5} = \frac{5}{4b^5} = \frac{5}{4} \left( \frac{a_0}{2Z} \right)^5 = \frac{5a_0^5}{128Z^5} \quad (\text{AX. 30})$$

Substituting Eq. (AX. 30) on Eq. (AX. 21), we get

$$E^{(1)} = (16) \left( \frac{Z}{a_0} \right)^6 \left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{5a_0^5}{128Z^5} \right) = \frac{5}{8} \frac{Z}{a_0} \left( \frac{e^2}{4\pi\epsilon_0} \right) = \frac{5Z}{4} \left[ \frac{1}{2} \frac{e^2}{(4\pi\epsilon_0)a_0} \right] = \frac{5 \times 2}{4} (13.6 \text{ eV}) = 34.0 \text{ eV} \quad (\text{AX. 31})$$

Finally,  $E = E^{(0)} + E^{(1)} = -108.8 \text{ eV} + 34.0 \text{ eV} = -74.8 \text{ eV}$

The experimental value is  $-79.0 \text{ eV}$ .

### APPLICATION TO A PARTICLE IN A ONE-DIMENSIONAL BOX

For a particle in a one-dimensional box ( $V = 0$  for  $0 < x < l$  and  $V = \infty$  elsewhere), we have

$$\psi_n = \sqrt{\frac{2}{l}} \sin \left( \frac{n\pi}{l} x \right) \quad \text{with} \quad E_n = \frac{n^2 h^2}{8ml^2}$$

Suppose the particle in the box is subjected to potential energy given by the expression

$$V = kx \quad \text{for } 0 < x < l \quad \text{and} \quad V = \infty \quad \text{elsewhere.}$$

In such a case, the perturbation is

$$H' = kx$$

The first-order energy correction is given by

$$\begin{aligned}
 E_n^{(1)} &= \int_0^l \psi_n |H'| \psi_n dx \\
 &= \frac{2}{l} \int_0^l \left[ \sin\left(\frac{n\pi}{l} x\right) |kx| \sin\left(\frac{n\pi}{l} x\right) \right] dx \\
 &= \frac{2k}{l} \int_0^l x \sin^2\left(\frac{n\pi}{l} x\right) dx = \frac{2k}{l} \int_0^l \frac{x}{2} \left[ 1 - \cos\left(\frac{2n\pi}{l} x\right) \right] dx \\
 &= \frac{2k}{l} \left[ \frac{x^2}{4} - \frac{(zero)}{2} \right] = \frac{kl}{2}
 \end{aligned}$$

The energy of the particle is given by

$$E_n = E_n^{(0)} + E_n^{(1)} = \frac{n^2 h^2}{8ml^2} + \frac{kl}{2}$$

### APPLICATION TO A PERTURBED HARMONIC OSCILLATOR

For a harmonic oscillator, we have

$$V = \frac{1}{2} k_f x^2$$

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp(-\alpha x^2/2); \quad \text{where } \alpha = \sqrt{k_f m}/(h/2\pi)$$

$$\text{and } E_0 = \frac{1}{2} h\nu_0 = \frac{1}{2} \frac{h}{2\pi} \sqrt{\frac{k_f}{m}}$$

Let the potential energy of a perturbed oscillator (may be called anharmonic oscillator) be given by

$$V = \frac{1}{2} k_f x^2 + k' x^3 + k'' x^4$$

where  $k'$  and  $k''$  are constants. In this case, the perturbation is

$$H' = k' x^3 + k'' x^4$$

The first-order correction to the ground-state energy is given by

$$\begin{aligned}
 E_0^{(1)} &= \int_{-\infty}^{+\infty} \psi_0 |H'| \psi_0 dx \\
 &= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{+\infty} (e^{-\alpha x^2/2} |k' x^3 + k'' x^4| e^{-\alpha x^2/2}) dx \\
 &= \left(\frac{\alpha}{\pi}\right)^{1/2} \left[ k' \int_{-\infty}^{+\infty} x^3 e^{-\alpha x^2} dx + k'' \int_{-\infty}^{+\infty} x^4 e^{-\alpha x^2} dx \right]
 \end{aligned}$$

$$\begin{aligned}
 &= \left(\frac{\alpha}{\pi}\right)^{1/2} \left[ k' (zero) + 2k'' \int_0^{+\infty} x^4 e^{-\alpha x^2} dx \right] \\
 &= \left(\frac{\alpha}{\pi}\right)^{1/2} \left[ 2k'' \left\{ \frac{3}{8\alpha^2} \left(\frac{\pi}{\alpha}\right)^{1/2} \right\} \right] = \frac{3k''}{4\alpha^2} = \frac{3k''(h/2\pi)^2}{4(k_f/m)}
 \end{aligned}$$

Hence, the energy of the perturbed oscillator is

$$E = E_0^{(0)} + E_0^{(1)} = \frac{1}{2} \frac{h}{2\pi} \sqrt{\frac{k_f}{m}} + \frac{3k''(h/2\pi)^2}{4(k_f/m)}$$

## ANNEXURE XI Proof of Variational Theorem

The proof of the variation theorem goes as follows.

The well-behaved approximate wave function  $\psi$  can be expanded in terms of a complete orthonormal set of eigenfunctions of the Hamiltonian operator  $H_{op}$ , that is

$$\psi = \sum_n C_n \phi_n$$

With this, we have

$$E = \frac{\langle \psi^* | H_{op} | \psi \rangle}{\langle \psi^* | \psi \rangle} = \frac{\langle (\sum_n C_n^* \phi_n^*) | H_{op} | (\sum_n C_n \phi_n) \rangle}{\langle (\sum_n C_n^* \phi_n^*) | (\sum_n C_n \phi_n) \rangle}$$

For an orthonormal set,

$$\langle \phi_n^* | \phi_n \rangle = 1 \quad \text{and} \quad \langle \phi_n^* | \phi_m \rangle = 0$$

With these, the above expression is reduced to

$$E = \frac{\sum_n C_n^* C_n E_n}{\sum_n C_n^* C_n}$$

Subtracting  $E_0$  from both sides, we get

$$E - E_0 = \frac{\sum_n C_n^* C_n E_n}{\sum_n C_n^* C_n} - E_0 = \frac{\sum_n C_n^* C_n (E_n - E_0)}{\sum_n C_n^* C_n}$$

Since  $E_n \geq E_0$  for all values of  $n$  and also  $C_n^* C_n \geq 0$ , we will have

$$E - E_0 \geq 0 \quad \text{or} \quad E \geq E_0$$

The variation function says that we can calculate the upper bound on  $E_0$  by using the appropriate trial wave function. The closer the function to the exact wave function, the closer the energy to the exact energy of the system.

## ANNEXURE XII The Variational Method

### ENERGY EVALUATION FOR A WAVE FUNCTION INVOLVING LINEARLY DEPENDENT VARIATION PARAMETERS

For simplicity, let a wave function involve two linearly dependent variation parameters, such that

$$\psi = C_1 \psi_1 + C_2 \psi_2$$

The energy expression is

$$E = \frac{\langle \psi | H_{op} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\langle (C_1 \psi_1 + C_2 \psi_2) | H_{op} | (C_1 \psi_1 + C_2 \psi_2) \rangle}{\langle (C_1 \psi_1 + C_2 \psi_2) | (C_1 \psi_1 + C_2 \psi_2) \rangle}$$

$$= \frac{C_1^2 H_{11} + C_2^2 H_{22} + 2C_1 C_2 H_{12}}{C_1^2 S_{11} + C_2^2 S_{22} + 2C_1 C_2 S_{12}}$$

where  $H_{ij} = \langle \psi_i | H_{op} | \psi_j \rangle$  and  $S_{ij} = \langle \psi_i | \psi_j \rangle$ .

The minimization of energy with respect to coefficients through the expression  $\partial E / \partial C_i = 0$  leads to the following secular equations.

$$\begin{cases} C_1(H_{11} - ES_{11}) + C_2(H_{12} - ES_{12}) = 0 \\ C_1(H_{21} - ES_{21}) + C_2(H_{22} - ES_{22}) = 0 \end{cases} \quad (\text{AXII.1})$$

These may be written in the determinant form as

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} \begin{vmatrix} C_1 \\ C_2 \end{vmatrix} = 0$$

To have nontrivial roots of energy, we set the secular determinant equal to zero, i.e.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \quad (\text{AXII.2})$$

which on opening gives

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{12} - ES_{12})(H_{21} - ES_{21}) = 0$$

Since  $H_{12} = H_{21}$  and  $S_{12} = S_{21}$ , we have

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{12} - ES_{12})^2 = 0$$

Knowing the values of  $H_{11}$ ,  $H_{22}$ ,  $H_{12}$ ,  $S_{11}$ ,  $S_{22}$  and  $S_{12}$ , one can solve the above quadratic expression in energy to get the two values of energy. Substituting these one by one in secular equations along with the normalization expression of  $\psi$  (which is  $C_1^2 S_{11} + C_2^2 S_{22} + 2C_1 C_2 S_{12} = 1$ ) provides the values of coefficients  $C_1$  and  $C_2$ .

**Note:** For a wave function involving  $n$  linearly dependent variation parameters (i.e.  $\psi = \sum_i C_i \psi_i$ ), the secular determinant takes the form of

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2n} - ES_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots & H_{nn} - ES_{nn} \end{vmatrix} = 0 \quad (\text{AXII.3})$$

For the orthonormal set of wave functions, for which  $S_{ij} = \delta_{ij}$ , the above determinant becomes

$$\begin{vmatrix} H_{11} - E & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22} - E & \dots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} & H_{n2} & \dots & H_{nn} - E \end{vmatrix} = 0 \quad (\text{AXII.4})$$

### APPLICATION TO A PARTICLE IN A ONE-DIMENSIONAL BOX

Let the wave function of a particle in a one-dimensional box ( $V = 0$  for  $0 < x < l$  and  $V = \infty$  elsewhere) be given as

$$\psi = C_1 \psi_1 + C_2 \psi_2$$

where  $\psi_1 = x(l-x)$  and  $\psi_2 = x^2(l-x)^2$ . To evaluate the energies, we determine the following integrals.

$$\begin{aligned} H_{11} &= \langle \psi_1 | H_{op} | \psi_1 \rangle = \left\langle x(l-x) \left| -\frac{\hbar^2}{8\pi^2 m} \frac{d^2}{dx^2} \right| x(l-x) \right\rangle \\ &= \left\langle x(l-x) \left| -\frac{\hbar^2}{8\pi^2 m} (-2) \right\rangle = 2 \left( \frac{\hbar^2}{8\pi^2 m} \right) \int_0^l (xl - x^2) dx \\ &= \left( \frac{\hbar^2}{8\pi^2 m} \right) \left( \frac{l^3}{3} \right) \\ S_{11} &= \langle \psi_1 | \psi_1 \rangle = \langle x(l-x) | x(l-x) \rangle \\ &= \int_0^l (l^2 x^2 + x^4 - 2lx^3) dx = \frac{l^5}{30} \end{aligned}$$

Proceeding similarly, we find that

$$\begin{aligned} H_{12} &= H_{21} = \left( \frac{\hbar^2}{8\pi^2 m} \right) \left( \frac{l^5}{15} \right) \\ S_{12} &= S_{21} = \frac{l^7}{140} \end{aligned}$$

$$H_{22} = \left( \frac{\hbar^2}{8\pi^2 m} \right) \left( \frac{2l^7}{105} \right)$$

$$S_{22} = \frac{l^9}{630}$$

With these, the secular determinant (Eq. AXII.2) becomes

$$\begin{vmatrix} \left( \frac{\hbar^2}{8\pi^2 m} \right) \left( \frac{l^3}{3} \right) - E \left( \frac{l^5}{30} \right) & \left( \frac{\hbar^2}{8\pi^2 m} \right) \left( \frac{l^5}{15} \right) - E \left( \frac{l^7}{140} \right) \\ \left( \frac{\hbar^2}{8\pi^2 m} \right) \left( \frac{l^5}{15} \right) - E \left( \frac{l^7}{140} \right) & \left( \frac{\hbar^2}{8\pi^2 m} \right) \left( \frac{2l^7}{105} \right) - E \left( \frac{l^9}{630} \right) \end{vmatrix} = 0$$

Let  $K = \hbar^2/(8\pi^2 ml^2)$ . With this, the above determinant becomes

$$\begin{vmatrix} Kl^5 \left( \frac{1}{3} - \frac{E'}{30} \right) & Kl^7 \left( \frac{1}{15} - \frac{E'}{140} \right) \\ Kl^7 \left( \frac{1}{15} - \frac{E'}{140} \right) & Kl^9 \left( \frac{2}{105} - \frac{E'}{630} \right) \end{vmatrix} = 0$$

where  $E' = E/K = 8\pi^2 ml^2 E/\hbar^2$ .

Opening the determinant, we get

$$K^2 l^{14} \left( \frac{1}{3} - \frac{E'}{30} \right) \left( \frac{2}{105} - \frac{E'}{630} \right) - K^2 l^{14} \left( \frac{1}{15} - \frac{E'}{140} \right)^2 = 0$$

Multiplying throughout by  $1260/K^2 l^{14}$ , we get

$$\begin{aligned} (420 - 42E')(24 - 2E') - (84 - 9E')^2 &= 0 \\ \text{or } 84(10 - E')(12 - E') - (84 - 9E')^2 &= 0 \\ \text{or } 84(120 - 22E' + E'^2) - (84 \times 84 + 81E'^2 - 84 \times 18E') &= 0 \\ \text{or } E'^2(84 - 81) + E'(84 \times 18 - 84 \times 22) + (84 \times 120 - 84 \times 84) &= 0 \\ \text{or } 3E'^2 - 336E' + 3024 &= 0 \\ \text{or } E'^2 - 112E' + 1008 &= 0 \end{aligned}$$

The roots of energy are

$$E' = \frac{112 \pm \sqrt{112^2 - 4 \times 1008}}{2} = \frac{112 \pm \sqrt{512}}{2} = \frac{112 \pm 92.26}{2}$$

$$E' = 102.13 \quad \text{and} \quad E' = 9.87$$

For the smaller root, we have

$$\left( \frac{8\pi^2 ml^2}{\hbar^2} \right) E = 9.87$$

or

$$E = \frac{9.87}{\pi^2} \left( \frac{\hbar^2}{8ml^2} \right)$$

Substituting  $E$  in secular equation (Eq. AXII.1), we get

$$C_1(H_{11} - ES_{11}) + C_2(H_{12} - ES_{12}) = 0$$

$$C_1 \left[ \frac{h^2}{8\pi^2 m} \frac{l^3}{3} - \left( \frac{9.87}{l^2} \frac{h^2}{8\pi^2 m} \right) \left( \frac{l^5}{30} \right) \right] + C^2 \left[ \frac{h^2}{8\pi^2 m} \frac{l^5}{15} - \left( \frac{9.87}{l^2} \frac{h^2}{8\pi^2 m} \right) \left( \frac{l^7}{140} \right) \right] = 0$$

This gives

$$C_1 \left( \frac{1}{3} - \frac{9.87}{30} \right) + C_2 l^2 \left( \frac{1}{15} - \frac{9.87}{140} \right) = 0$$

$$\text{i.e. } C_1 = C_2 l^2 (1.61/1.62)$$

Substituting this in the normalization expression

$$C_1^2 S_{11} + C_2^2 S_{22} + 2C_1 C_2 S_{12} = 1$$

we get

$$C_2^2 l^4 \left( \frac{1.61}{1.62} \right)^2 \left( \frac{l^5}{30} \right) + C_2^2 \left( \frac{l^9}{630} \right) + 2C_2^3 l^2 \left( \frac{1.61}{1.62} \right) \left( \frac{l^7}{140} \right) = 1$$

$$l^9 C_2^2 \left[ \left( \frac{1.61}{1.62} \right)^2 \frac{1}{3} + \frac{1}{63} + \left( \frac{1.61}{1.62} \right) \frac{1}{7} \right] = 1 \Rightarrow C_2 = 1.433/\sqrt{l^9}$$

$$C_1 = C_2 l^2 (1.61/1.62) = (1.443/\sqrt{l^9}) l^2 (1.61/1.62) = 1.424/\sqrt{l^5}$$

Hence, the normalized wave function is

$$\psi = \frac{1.424}{\sqrt{l^5}} x(l-x) + \frac{1.433}{\sqrt{l^9}} x^2(l-x)^2$$

## NUCLEAR CHARGE OF HELIUM ATOM AS A VARIATIONAL PARAMETER

The Hamiltonian operator of helium atom is

$$H_{op} = -\frac{h^2}{8\pi^2 m} \nabla_1^2 - \frac{h^2}{8\pi^2 m} \nabla_2^2 - \frac{Ze^2}{(4\pi\epsilon_0)r_1} - \frac{Ze^2}{(4\pi\epsilon_0)r_2} + \frac{e^2}{(4\pi\epsilon_0)r_{12}} \quad (\text{AXII.3})$$

The ground-state normalized wave function is

$$\begin{aligned} \psi &= \psi_1 \psi_2 = (R_{100} \theta_{0,0} \theta_{0,1}) (R_{100} \theta_{0,0} \theta_{0,2}) \\ &= \left[ 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr_1/a_0} \cdot \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2\pi}} \right] \left[ 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr_2/a_0} \cdot \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2\pi}} \right] \\ &= \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 e^{-Zr_1/a_0} e^{-Zr_2/a_0} \quad (\text{AXII.4}) \end{aligned}$$

Taking the nuclear charge as the variational parameter, we write  $Z$  as  $Z'$  (known as effective nuclear charge). Thus

$$\psi = \frac{1}{\pi} \left( \frac{Z'}{a_0} \right)^3 e^{-Z'r_1/a_0} e^{-Z'r_2/a_0} \quad (\text{AXII.5})$$

The Hamiltonian operator can be written as

$$\begin{aligned} H_{op} &= \left[ -\frac{h^2}{8\pi^2 m} \nabla_1^2 - \frac{Z'e^2}{(4\pi\epsilon_0)r_1} \right] + \left[ -\frac{h^2}{8\pi^2 m} \nabla_2^2 - \frac{Z'e^2}{(4\pi\epsilon_0)r_2} \right] \\ &\quad + \frac{(Z'-Z)e^2}{(4\pi\epsilon_0)r_1} + \frac{(Z'-Z)e^2}{(4\pi\epsilon_0)r_2} + \frac{e^2}{(4\pi\epsilon_0)r_{12}} \\ &= \hat{H}_1 + \hat{H}_2 + \frac{(Z'-Z)e^2}{(4\pi\epsilon_0)r_1} + \frac{(Z'-Z)e^2}{(4\pi\epsilon_0)r_2} + \frac{e^2}{(4\pi\epsilon_0)r_{12}} \quad (\text{AXII.6}) \end{aligned}$$

The electronic energy of the atom is given by

$$\begin{aligned} E &= \langle \psi | H_{op} | \psi \rangle \\ &= \langle \psi_1 \psi_2 | \hat{H}_1 + \hat{H}_2 + \frac{(Z'-Z)e^2}{(4\pi\epsilon_0)r_1} + \frac{(Z'-Z)e^2}{(4\pi\epsilon_0)r_2} + \frac{e^2}{(4\pi\epsilon_0)r_{12}} | \psi_1 \psi_2 \rangle \\ &= \langle \psi_1 | \hat{H}_1 | \psi_1 \rangle \langle \psi_2 | \psi_2 \rangle + \langle \psi_2 | \hat{H}_2 | \psi_2 \rangle \langle \psi_1 | \psi_1 \rangle \\ &\quad + \langle \psi_1 | \frac{(Z'-Z)e^2}{(4\pi\epsilon_0)r_1} | \psi_1 \rangle \langle \psi_2 | \psi_2 \rangle + \langle \psi_2 | \frac{(Z'-Z)e^2}{(4\pi\epsilon_0)r_2} | \psi_2 \rangle \langle \psi_1 | \psi_1 \rangle \\ &\quad + \langle \psi_1 \psi_2 | \frac{e^2}{(4\pi\epsilon_0)r_{12}} | \psi_1 \psi_2 \rangle \end{aligned}$$

Since  $\psi_1$  and  $\psi_2$  are normalized, we get

$$\begin{aligned} E &= \langle \psi_1 | \hat{H}_1 | \psi_1 \rangle + \langle \psi_2 | \hat{H}_2 | \psi_2 \rangle + \langle \psi_1 | \frac{(Z'-Z)e^2}{(4\pi\epsilon_0)r_1} | \psi_1 \rangle \\ &\quad + \langle \psi_2 | \frac{(Z'-Z)e^2}{(4\pi\epsilon_0)r_2} | \psi_2 \rangle + \langle \psi_1 \psi_2 | \frac{e^2}{(4\pi\epsilon_0)r_{12}} | \psi_1 \psi_2 \rangle \quad (\text{AXII.7}) \end{aligned}$$

Now

$$\langle \psi_1 | \hat{H}_1 | \psi_1 \rangle = -Z'^2 E_{1s(H)}$$

$$\langle \psi_2 | \hat{H}_2 | \psi_2 \rangle = -Z'^2 E_{1s(H)}$$

$$\begin{aligned} \langle \psi_1 | \frac{(Z'-Z)e^2}{(4\pi\epsilon_0)r_1} | \psi_1 \rangle &= \frac{1}{\pi} \left( \frac{Z'}{a_0} \right)^3 \int_0^\infty \int_0^\pi e^{-Z'r_1/a_0} \left[ \frac{(Z'-Z)e^2}{(4\pi\epsilon_0)r_1} \right] e^{-Z'r_1/a_0} \\ &\quad \times r_1^2 dr_1 \int_0^{2\pi} \sin \theta_1 d\theta_1 \int_0^\pi d\phi \end{aligned}$$

$$\begin{aligned}
 &= \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 \frac{(Z-Z)^2 e^2}{(4\pi\epsilon_0)} \left( \int_0^\infty r_1 e^{-2Zr_1/a_0} dr_1 \right) \left( \int_0^\pi \sin\theta d\theta \right) \left( \int_0^{2\pi} d\phi \right) \\
 &= \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 \frac{(Z-Z)^2 e^2}{(4\pi\epsilon_0)} \left[ \frac{1}{(2Z/a_0)^2} \right] [2] [2\pi] \\
 &= 2Z'(Z'-Z) \left[ \frac{1}{2} \frac{e^2}{(4\pi\epsilon_0)a_0} \right] = 2Z'(Z'-Z)E_{\text{is(H)}}
 \end{aligned}$$

Similarly,

$$\left\langle \psi_2 \left| \frac{(Z'-Z)e^2}{(4\pi\epsilon_0)r_2} \right| \psi_2 \right\rangle = 2Z'(Z'-Z)E_{\text{is(H)}}$$

As derived in the perturbation theory, we will have

$$\left\langle \psi_1 \psi_2 \left| \frac{e^2}{(4\pi\epsilon_0)r_{12}} \right| \psi_1 \psi_2 \right\rangle = \frac{5Z'}{4} E_{\text{is(H)}} \quad (\text{Eq. AX.31})$$

With these integrals, Eq. (AXII. 7) becomes

$$\begin{aligned}
 E &= -Z'^2 E_{\text{is(H)}} - Z'^2 E_{\text{is(H)}} + 2Z'(Z'-Z)E_{\text{is(H)}} \\
 &\quad + 2Z'(Z'-Z)E_{\text{is(H)}} + \frac{5Z'}{4} E_{\text{is(H)}} \\
 &= \left[ -2Z'^2 + 4Z'(Z'-Z) + \frac{5Z'}{4} \right] E_{\text{is(H)}} = \left[ 2Z'^2 - 4Z'Z + \frac{5Z'}{4} \right] E_{\text{is(H)}}
 \end{aligned}$$

Since  $Z = 2$ , we have

$$E = \left( 2Z'^2 - \frac{27}{4} Z' \right) E_{\text{is(H)}} \quad (\text{AXII. 8})$$

To minimize  $E$ , we set  $dE/dZ' = 0$ . This gives

$$\left( 4Z' - \frac{27}{4} \right) E_{\text{is(H)}} = 0$$

Hence  $Z' = 27/16$

Substituting  $Z' = 27/16$  in Eq. (AXII. 8), we get

$$\begin{aligned}
 E_{\text{min}} &= \left[ 2 \left( \frac{27}{16} \right)^2 - \left( \frac{27}{4} \right) \left( \frac{27}{16} \right) \right] E_{\text{is(H)}} = \left( \frac{27}{16} \right) \left( \frac{27}{8} - \frac{27}{4} \right) E_{\text{is(H)}} \\
 &= - \left( \frac{27}{16} \right) \left( \frac{27}{8} \right) (13.6 \text{ eV}) \\
 &= -77.46 \text{ eV}
 \end{aligned}$$

The experimental value is  $-79.0 \text{ eV}$ .

## SLATER RULES FOR EFFECTIVE NUCLEAR CHARGE

For helium atom, we have  $Z^* = 27/16$

This may be written as  $Z^* = Z - 5/16$

where the constant  $5/16 (= 0.3125)$  is known as screening contribution. The nuclear charge observed by electron 1 in 1s orbital is  $27/16$  instead of 2 due to the screening of nuclear charge by electron 2 in the same orbital, i.e. the electron 2 screens  $5/16$  of charge for electron 1 and vice versa. In general, we can write

$$Z_i^* = Z - \sum_{j \neq i} s_{ji}$$

where the sum is over all the occupied spin orbitals other than the one considered.

The empirical rules, known as Slater's rule, are available to determine the effective nuclear charge as observed by an electron in an atom. The screening contributions may be determined based on the following groups of orbitals.

$$(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p)$$

The rules to be followed are as follows.

1. For the spin orbital  $j$  from a group after that of the spin orbital  $i$ , the value of  $s_{ji} = 0$
2. For the spin orbital  $j$  from the same group as that of the spin orbital  $i$ , the value of  $s_{ji} = 0.35$
3. For the spin orbital  $j$  from a group appearing before that of the spin orbital  $i$ , the value of  $s_{ji}$  is:
  - (i)  $s_{ji} = 1$  if  $j$  is a d or f orbital
  - (ii)  $s_{ji} = 0.85$  if  $j$  is a s or p orbital when  $n_j = n_i - 1$ , otherwise  $s_{ji} = 1$ .

### Examples

${}^8\text{O}$ : Electronic configuration:  $(1s)^2 (2s)^2 (2p)^4$

Grouping of the orbitals:  $(1s)^2 (2s, 2p)^6$

For valence electron:

$$S = \sum_{j \neq i} s_{ji} = (2 \times 0.85) + (5 \times 0.35) = 3.45$$

$$Z^* = Z - S = 8 - 3.45 = 4.55$$

${}_{25}\text{Mn}$ : Electronic configuration:  $(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (3d)^5 (4s)^2$

Grouping of the orbitals:  $(1s)^2 (2s, 2p)^8 (3s, 3p)^8 (3d)^5 (4s)^2$

For 4s electron:

$$S = (10 \times 1.0) + (13 \times 0.85) + (1 \times 0.35) = 21.40$$

$$Z^* = Z - S = 25 - 21.4 = 3.6$$

For 3d electron:

$$S = (18 \times 1.0) + (4 \times 0.35) = 19.4$$

$$Z^* = 25 - 19.4 = 5.6$$



# 2 Theories of Covalent Bond

## 2.1 INTRODUCTION

The qualitative picture for the formation of a covalent bond was provided by G.N. Lewis who described a covalent bond formation due to the sharing of electron pairs between atoms. This sharing of electron pairs helps each atom acquire a stable electronic configuration. The stability of a diatomic molecule with respect to the individual atoms can be understood qualitatively on the basis of electrostatic interactions. The shared electron pair lies in the central region of the two atoms. This arrangement besides decreasing the electrostatic repulsion between the two nuclei, results in the maximum interaction between the nuclei and electrons. Consequently, in a molecule the electrostatic attraction terms predominate over the repulsion terms which results in the release of energy when a molecule is formed from the atoms. Thus, a molecule is energetically more stable than the individual atoms.

The quantitative aspects for the formation of a covalent bond have been provided by quantum mechanics. According to the latter, a covalent molecule may be described by means of a wave function which describes the behaviour of the electrons under the influence of all nuclei in the molecule and all other electrons in the molecule. Thus, in principle, all that we have to do is to write the Schrödinger equation for the molecule and then solve this equation for various allowed eigenvalues and eigenfunctions. However, like many-electron atoms, only approximate methods can be employed to solve the Schrödinger equation.

## 2.2 EXPRESSION OF SCHRÖDINGER EQUATION

The Schrödinger equation for a molecule containing  $N$  nuclei and  $n$  electrons is

$$H_{op} \Psi = E \Psi \quad (2.2.1)$$

where the Hamiltonian operator is given by

$$H_{op} = T + V = \left( -\sum_{i=1}^N \frac{h^2}{8\pi^2 M_i} \nabla_i^2 - \sum_{j=1}^n \frac{h^2}{8\pi^2 m_e} \nabla_j^2 \right) + (V_{ne} + V_{ec} + V_{nn}) \quad (2.2.2)$$

The terms  $V_{ne}$ ,  $V_{ec}$  and  $V_{nn}$  describe, respectively, the nucleus-electron, electron-electron, and nucleus-nucleus interaction terms. These are given by

$$V_{ne} = -\sum_{i=1}^N \sum_{j=1}^n \frac{Z_i e^2}{(4\pi\epsilon_0) r_{ij}} \quad (2.2.3a)$$

$$V_{ec} = \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n \frac{e^2}{(4\pi\epsilon_0) r_{ij}} \quad (2.2.3b)$$

$$V_{nn} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{Z_i Z_j e^2}{(4\pi\epsilon_0) r_{ij}} \quad (2.2.3c)$$

where  $e$  is equal to the electronic charge. The function  $\Psi$  depends on the coordinates of both electrons and nuclei.

## 2.3 BORN-OPPENHEIMER APPROXIMATION

The term representing the nuclear motion in the Hamiltonian operator (Eq. 2.2.2) can be removed with the help of Born-Oppenheimer approximation. This is based on the fact that the electrons being much lighter than the nuclei, make many traverses of the space available to them while the nuclei change their positions only slightly. Hence, the translational energy of the molecule as a whole may be considered separately and while evaluating the electronic energy, the various nuclei may be considered fixed in space with constant internuclear distances.

The above approximation is achieved by writing the total wave function as the product of electronic wave function and the nuclear wave function. The former depends on the coordinates of the electrons as well as those of nuclei. The latter depends only on the coordinates of nuclei. Thus, we have

$$\Psi = \psi_e \psi_n \quad (2.3.1)$$

The Hamiltonian operator of Eq. (2.2.2) may be written as

$$H = H_e + H_n \quad (2.3.2)$$

$$\text{where } H_e = -\sum_{i=1}^n \frac{h^2}{8\pi^2 m_e} \nabla_i^2 + V_{ec} + V_{nn} + V_{ee}$$

$$H_n = -\sum_{i=1}^N \frac{h^2}{8\pi^2 M_i} \nabla_i^2$$

The electronic wave function  $\psi_e$  is defined by

$$H_e \psi_e = E_e \psi_e \quad (2.3.3)$$

and the nuclear wave function  $\psi_n$  by

$$(H_n + E_e) \psi_n = E \psi_n \quad (2.3.4)$$

It may be mentioned here that  $E_e$  depends on the coordinates of nuclei. Since the molecule is considered to be fixed in space, the energy  $E_e$  represents the electronic energy for the fixed coordinates of nuclei (i.e. fixed internuclear distances). In Eq. (2.3.4), the Hamiltonian operator for nuclear motion includes the nuclear kinetic energy operator and the electronic energy function, so the symbol  $E$  represents the total energy of the molecule, i.e. nuclear energy plus electronic energy.

## 2.4 TWO APPROACHES FOR APPROXIMATE SOLUTION OF SCHRÖDINGER EQUATION

The electronic energy  $E_e$  for the given internuclear distances may be calculated by solving the Schrödinger equation as given by Eq. (2.3.3):

$$H_e \psi_e = E_e \psi_e \quad (2.4.1)$$

However, the above equation cannot be solved exactly even if the internuclear distances are held constant. This is due to the presence of electron-electron repulsion terms in the Hamiltonian operator. Consequently, various approaches have been developed for the approximate solution of Schrödinger equation. Of these, the following two approaches have been widely used.

- The molecular orbital (MO) method developed by Hund, Mulliken, Lennard-Jones and Hückel.
- The valence bond (VB) method developed by Heitler and London, Slater and Pauling.

In the molecular orbital approach, we look at the molecule as a collection of nuclei and electrons. We build up molecular orbitals for collection of nuclei and then assign electrons to them. The valence orbital approach, which was developed prior to the molecular orbital approach, is very similar to the classical chemical concept of valence bond between two atoms and to the electron-pair bond postulated by Lewis. In this method, the molecule is considered as a collection of atoms and then the interactions between different atoms are considered. Hence, the two approaches differ in the choice of trial wave functions whose parameters are then optimized by the variation method. In their elementary forms, both these methods give results that are crude from a quantitative point of view. However, both the methods can be refined by using better trial functions. Both the methods, when carried out up to their extreme refinements, produce identical results.

### Trial Wave Function in MO Method

The basic principles of MO method are very similar to those of the self-consistent field method for atoms. These are:

- Each electron in a molecule is described by a wave function, known as the molecular orbital. These molecular orbitals extend over the entire region of the molecule, i.e. they are polycentric.
- The significance of molecular orbital is the same as that of atomic orbital. Thus,  $\psi \psi^* d\tau$  represents the relative probability of finding an electron in the volume element  $d\tau$ . Alternatively,  $\psi \psi^* d\tau$  represents the charge density in the volume element  $d\tau$ .
- Each MO may be represented by drawing contours of constant  $\psi$  or  $\psi^2$  or by drawing a boundary surface which includes the majority of charge cloud.
- Each MO is associated with a definite energy which may be calculated by solving the appropriate Schrödinger equation.
- The allocation of electrons to the various molecular orbitals of a molecule is done following the aufbau and Pauli exclusion principles.

### Approximation of Linear Combination of Atomic Orbitals

#### Physical Significance of Coefficients in LCAO MO

One of the most important ways of constructing molecular orbital is the scheme based on the approximation of *linear combination of atomic orbitals*, abbreviated as LCAO approximation. The choice of LCAO can be rationalized by taking an example of a diatomic molecule AB. If the electron is in the neighbourhood of nucleus A, the influence of nucleus B is expected to be small, and hence the MO, say, for example, the ground-state MO, in this region should be similar to the ground-state atomic orbital (AO) of atom A. Similarly, if the electron is in the neighbourhood of nucleus B, the MO will look like very similar to the AO of the atom B. Thus, the form of the MO should be such that it has characteristics possessed separately by  $\psi_A$  and  $\psi_B$ ; i.e. the MO should be reducible to AOs in the extreme cases. The only choice is to take MO as the linear combination of atomic orbitals. Mathematically, it is written as

$$\psi_{MO} = C_1 \psi_A + C_2 \psi_B \quad (2.4.2)$$

where  $C_1$  and  $C_2$  are constants which, respectively, are the weighting coefficients for the functions  $\psi_A$  and  $\psi_B$ . In the extreme situations mentioned above, we will have  $C_1 = 1$  and  $C_2 = 0$ ; when the electron is near to the nucleus A and  $C_1 = 0$  and  $C_2 = 1$ ; when the electron is near to the nucleus B.

For any other situation  $C_1$  and  $C_2$  may have identical or different values depending upon the nature of atoms and the associated wave functions  $\psi_A$  and  $\psi_B$ .

Since the electron distribution is given by the square of the wave function, the electron distribution for the function given by Eq. (2.4.2) is

$$\psi_{MO}^2 = C_1^2 \psi_A^2 + C_2^2 \psi_B^2 + 2C_1 C_2 \psi_A \psi_B$$

The terms  $C_1^2$  and  $C_2^2$  describe the probabilities of finding the electron in the orbitals  $\psi_A$  and  $\psi_B$ , respectively, and the coefficient  $2C_1 C_2$  describes the electron probability density of orbitals  $\psi_A$  and  $\psi_B$  overlapping in the bond region.

The normalization criterion applied to  $\psi_{MO}$  gives

$$\int \psi_{MO}^2 d\tau = 1 = C_1^2 \int \psi_A^2 d\tau + C_2^2 \int \psi_B^2 d\tau + 2C_1 C_2 \int \psi_A \psi_B d\tau$$

Assuming atomic orbitals to be normalized, we get

$$C_1^2 + C_2^2 + 2C_1 C_2 S_{AB} = 1$$

where  $S_{AB}$  is the overlap integral between the orbitals  $\psi_A$  and  $\psi_B$ . In the zero-overlap approximation ( $S_{AB} = 0$ ) the normalization condition is

$$C_1^2 + C_2^2 = 1$$

In the zero-overlap approximation,  $C_1^2$  and  $C_2^2$  give directly the electronic charge densities associated with the nuclei A and B, respectively. In the nonzero-overlap approximation, the coefficients  $C_1^2$  (or  $C_2^2$ ) and  $2C_1 C_2$  are known as *atomic-orbital* and *overlap densities*, respectively. To get the relative distribution of charge on the two atoms, *Mulliken gross atomic population numbers* are evaluated by adding the term  $(1/2)(2C_1 C_2 S_{AB})$  to the atomic orbital densities. Thus, the gross atomic

populations on atoms A and B due to one electron in the molecular orbital  $\psi_{MO}$  are  $C_1^2 + C_1 C_2 S_{AB}$  and  $C_2^2 + C_1 C_2 S_{AB}$ , respectively.

The values of  $C_1$  and  $C_2$  are determined by the variation method, subjected to the condition of normalization, written as

$$\int \psi_{MO}^2 d\tau = 1 \quad (2.4.3)$$

It is not necessary that we include only one atomic orbital from each atom. In general, we can include any number of atomic orbitals belonging to the different atoms and thus write MO as

$$\psi_{MO} = \sum_i C_i \psi_i \quad (2.4.4)$$

Larger the number of atomic orbitals included, better the molecular orbital. The effective combination of different AOs is determined by the values of coefficients  $C_i$ . While evaluating  $C_i$ 's, it may be found that for one combination, many of  $C_i$  have zero values or small values and only a few (may be two or three or four) have significant values. Thus, a larger combination of atomic orbitals is, in fact, equivalent to the combination of a few atomic orbitals.

In general, the combination of AOs are determined by the following factors:

1. The combination is better if the energies of  $\psi_A$  and  $\psi_B$  in their respective atoms have comparable values. To illustrate the point, we may take an example of  $H_2$  molecule, written as  $H_A - H_B$ . The combination of  $1s(H_A)$  and  $1s(H_B)$  or  $2s(H_A)$  and  $2s(H_B)$  or  $2p_x(H_A)$  and  $2p_x(H_B)$ , and so on will be the most effective, i.e. the coefficients  $C_A$  and  $C_B$  are expected to have comparable values (in fact, both of them will have the same value because atoms A and B are identical and the orbital in combination have identical energies). The combination  $1s(H_A) + 2s(H_B)$ ,  $1s(H_A) + 3s(H_B)$ , etc., may not be effective as the energies of involved AOs have a large difference.

2. The combination is better if the charge clouds of  $\psi_A$  and  $\psi_B$  overlap each other as much as possible.

3. Only those orbitals combine which have the same symmetry relative to the molecular axis. Thus,  $1s(H_A)$  and  $2p_x(H_B)$  orbitals will not mix with each other as they have different symmetry.

The above factors can be easily explained by evaluating the trial function

$$\psi_{MO} = C_1 \psi_A + C_2 \psi_B \quad (2.4.5)$$

and the energy associated with this orbital. It will be shown in the next section that the coefficients and energies of the two molecular orbitals formed by the combination of the two atomic orbitals  $\psi_A$  and  $\psi_B$  will be given by the following two simultaneous linear equations:

$$C_1(\alpha_A - E) + C_2(\beta_{AB} - ES_{AB}) = 0 \quad (2.4.6a)$$

$$C_1(\beta_{AB} - ES_{AB}) + C_2(\alpha_B - E) = 0 \quad (2.4.6b)$$

where  $\alpha_A$  and  $\alpha_B$  represent the energies of electron in the isolated atoms,  $\beta_{AB}$  is the resonance integral given by  $\int \psi_A H_{op} \psi_B d\tau$  and  $S_{AB}$  is the overlap integral (defined as  $\int \psi_A \psi_B d\tau$ ) which measures the extent of overlapping of the two orbitals. It will also be shown that the energies of molecular orbitals will be given by the following quadratic equation:

$$(\alpha_A - E)(\alpha_B - E) - (\beta_{AB} - ES_{AB})^2 = 0$$

$$\text{i.e. } (\alpha_A - E)(\alpha_B - E) = (\beta_{AB} - ES_{AB})^2 \quad (2.4.7)$$

To prove condition (1), we assume that  $\alpha_A$  is very much smaller than  $\alpha_B$ . Since the energy of an orbital depends on its size, it follows that the size of  $\psi_A$  will be much smaller than  $\psi_B$ . Consequently both  $S_{AB}$  and  $\beta_{AB}$  will have low values and thus the second term of Eq. (2.4.7) will have a small value. In order that the first term of Eq. (2.4.7) also has a small value, it is expected that either  $\alpha_A - E$  or  $\alpha_B - E$  has a small value. If we assume that  $\alpha_A - E$  is small, then the approximate solution of Eq. (2.4.7) can be achieved by putting  $E = \alpha_A$  in the term  $\alpha_B - E$ . Thus, we get

$$(\alpha_A - E)(\alpha_B - \alpha_A) = (\beta_{AB} - \alpha_A S_{AB})^2$$

$$\text{Hence } E_+ \simeq \alpha_A - \frac{(\beta_{AB} - \alpha_A S_{AB})^2}{\alpha_B - \alpha_A} \quad (2.4.8)$$

Similarly if we repeat the process for  $E \simeq \alpha_B$ , we get

$$E_- = \alpha_B + \frac{(\beta_{AB} - \alpha_B S_{AB})^2}{\alpha_B - \alpha_A} \quad (2.4.9)$$

Since  $\alpha_B \gg \alpha_A$ , it follows that  $E_+$  and  $E_-$  will have values very close to  $\alpha_A$  and  $\alpha_B$ , respectively.

From Eq. (2.4.6), we find that

$$\frac{C_1}{C_2} = - \frac{\beta_{AB} - E_+ S_{AB}}{\alpha_A - E_+} \quad \text{for } \psi_+ \text{ orbital}$$

$$\text{and } \frac{C_2}{C_1} = - \frac{\beta_{AB} - E_- S_{AB}}{\alpha_B - E_-} \quad \text{for } \psi_- \text{ orbital}$$

Since  $E_+$  and  $E_-$  are very close to  $\alpha_A$  and  $\alpha_B$ , respectively, it follows that

$$\frac{C_1}{C_2} \text{ will have a large value in } \psi_+ \text{ orbital}$$

$$\text{and } \frac{C_2}{C_1} \text{ will have a large value in } \psi_- \text{ orbital.}$$

The above facts imply that the mixing between  $\psi_A$  and  $\psi_B$  is very small. This proves the condition (1) listed above.

**Proof of Condition (2)** The condition (2) follows directly from Eqs (2.4.8) and (2.4.9). If the two atomic orbitals  $\psi_A$  and  $\psi_B$  do not overlap, then both  $S_{AB}$  and  $\beta_{AB}$  will have zero values.

Thus  $E_+ = \alpha_A$  and  $E_- = \alpha_B$ , i.e. no effective combination between  $\psi_A$  and  $\psi_B$  will occur. In other words, if we want an effective combination, the integrals  $S_{AB}$  and  $\beta_{AB}$  must be nonzero. This conclusion is often referred to as the *criterion of maximum overlapping*.

### Proof of Condition (3)

Proof of condition (3) follows directly from the fact that  $S_{AB}$  has a zero value for the orbitals having different symmetry about the molecular axis. For example,  $(1s)_A$  is completely symmetrical and  $(2p_z)_B$  or  $(2p_y)_B$  is antisymmetrical (positive lobe on one side and negative lobe on the other side). Because of different signs of  $2p_z$  orbital, the integral  $S_{AB}$  has a zero value even though the two orbitals overlap as shown in Fig. 2.4.1.

Hence, no mixing between such orbitals can occur.

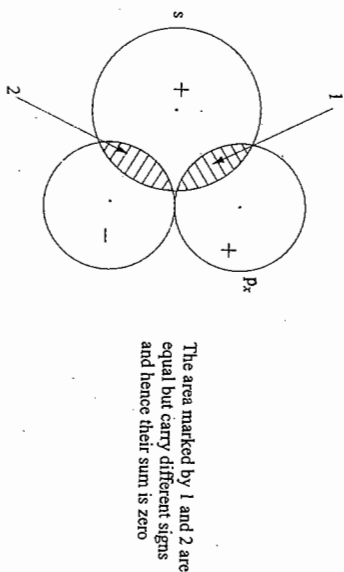


Fig. 2.4.1 Overlapping between s-type and p<sub>z</sub>-type orbitals

### Example 2.4.1

Given that the electronic charge densities on the two hydrogen atoms of  $H_2^+$  molecule are equal, derive the values of  $C_1$  and  $C_2$  of the ground-state molecular orbital as given by Eq. (2.4.2) in the zero- and nonzero overlap approximations. Given:  $S_{AB} = 0.4584$ .

The  $H_2^+$  molecule contains 1 electron. Thus, in the zero-overlap approximation, we may write

$$C_1^2 = C_2^2 = 0.5$$

Thus  $C_1 = C_2 = \sqrt{0.5} = 0.707$

Hence, the form of molecular orbital is

$$\psi_{MO} = 0.707 \psi_{1s(A)} + 0.707 \psi_{1s(B)}$$

In the nonzero-overlap approximation, we will have

$$C_1^2 + C_1 C_2 S_{AB} = 0.5$$

$$C_2^2 + C_1 C_2 S_{AB} = 0.5$$

Since  $C_1$  and  $C_2$  will be identical in  $H_2^+$  (because of symmetrical nature), we have

$$C_1^2 + C_1^2(0.4584) = 0.5$$

### Example 2.4.2

#### Solution

$$\text{or } C_1^2 = \frac{0.5}{1 + 0.4584} = 0.343$$

$$\text{or } C_1 = 0.586$$

Thus, the  $\psi_{MO}$  is given by

$$\psi_{MO} = 0.586 \psi_{1s(A)} + 0.586 \psi_{1s(B)}$$

One of the molecular orbitals of a diatomic molecule BA is given by

$$\psi_{MO} = C_1 \psi_{1s(A)} + C_2 \psi_{2s(B)} + C_3 \psi_{2p_z(B)}$$

Given that an electron spends 67.0, 21.6 and 11.4 per cents of its time in the orbitals  $\psi_{1s(A)}$ ,  $\psi_{2s(B)}$  and  $\psi_{2p_z(B)}$  respectively, determine the form of the ground-state wave function  $\psi_{MO}$  in the zero-overlap approximation.

We are given that

$$C_1^2 = 0.670; \quad C_2^2 = 0.216 \quad \text{and} \quad C_3^2 = 0.114$$

Taking the square roots, we get

$$C_1 = 0.818; \quad C_2 = 0.465 \quad \text{and} \quad C_3 = 0.337$$

Hence, the form of ground-state wave function is

$$\psi_{MO} = 0.818 \psi_{1s(A)} + 0.465 \psi_{2s(B)} + 0.337 \psi_{2p_z(B)}$$

(Note: For the ground-state wave function, all the coefficients will have positive values.)

### Trial Wave Function in VB Method

As indicated earlier, in the VB method, we consider a molecule as a collection of atoms. To know how a trial function in VB method is chosen, we consider the hydrogen molecule for a specific example. In a system where two atoms are very far apart with no interaction with each other, the total energy of the system will be equal to the sum of the energies of the separate atoms. We may treat this system separately as

$$E_{\text{total}} = E_A^{(1)} + E_B^{(2)} \quad (2.4.10)$$

$$= \langle \psi_A(1) | H_A | \psi_A(1) \rangle + \langle \psi_B(2) | H_B | \psi_B(2) \rangle$$

where  $\psi_A(1)$  and  $H_A$  are the wave function for the electron 1 and the Hamiltonian operator respectively, associated with atom A and  $\psi_B(2)$  and  $H_B$  are those of electron 2 associated with atom B.

The above assembly may equally be represented by writing the wave-function and Hamiltonian operator as

$$\psi = \psi_A(1) \psi_B(2) \quad (2.4.11)$$

$$H_{\text{op}} = H_A + H_B \quad (2.4.12)$$

Thus  $E_{\text{total}} = \langle \psi | H_{\text{op}} | \psi \rangle$

$$= \langle \psi_A(1) \psi_B(2) | H_A + H_B | \psi_A(1) \psi_B(2) \rangle$$

$$= \langle \psi_A(1) | H_A | \psi_A(1) \rangle \langle \psi_B(2) | \psi_B(2) \rangle$$

$$+ \langle \psi_B(2) | H_B | \psi_B(2) \rangle \langle \psi_A(1) | \psi_A(1) \rangle$$

Since the functions are normalized, the above expression becomes

$$E_{\text{total}} = \langle \psi_A(1) | H_A | \psi_A(1) \rangle + \langle \psi_B(2) | H_B | \psi_B(2) \rangle \\ = E_A^{(1)} + E_B^{(2)}$$

Now consider that the two atoms are brought together to a distance  $r_{AB}$ , where they interact with each other. The Hamiltonian operator of the system will be given by

$$H_{\text{op}} = \left( -\frac{\hbar^2}{8\pi^2 m} \nabla_1^2 - \frac{e^2}{(4\pi\epsilon_0)r_{A1}} \right) + \left( -\frac{\hbar^2}{8\pi^2 m} \nabla_2^2 - \frac{e^2}{(4\pi\epsilon_0)r_{B2}} \right) \\ + \left( -\frac{e^2}{(4\pi\epsilon_0)r_{A2}} - \frac{e^2}{(4\pi\epsilon_0)r_{B1}} + \frac{e^2}{(4\pi\epsilon_0)r_{12}} + \frac{e^2}{(4\pi\epsilon_0)r_{AB}} \right) \\ = H_A + H_B + H' \quad (2.4.13)$$

In VB method, we say that the wave function of the above system has the form as that of atoms very far apart (Eq. 2.4.10), i.e.  $\psi = \psi_A(1)\psi_B(2)$ . But when the two atoms are close together, we cannot distinguish electron 1 from electron 2. We may have another combination where electron 1 is considered to be associated with atom B and electron 2 with atom A, for which we write the wave function as  $\psi_A(2)\psi_B(1)$ . Hence the region where interaction occurs, Heitler and London suggested that the wave function may be taken as the linear combination of the two degenerate functions  $\psi_A(1)\psi_B(2)$  and  $\psi_A(2)\psi_B(1)$ , i.e.

$$\psi_{\text{VB}} = C_1 \psi_A(1)\psi_B(2) + C_2 \psi_A(2)\psi_B(1) \quad (2.4.14)$$

The constants  $C_1$  and  $C_2$  are determined with help of variation method.

The wave functions in Eq. (2.4.14) represent covalent structures as each bonded atom contains one electron. The wave function as given by Eq. (2.4.14) may be improved upon by including the wave functions corresponding to the ionic structures where both the electrons belong either to atom A or to atom B. Thus, we write

$$\psi_{\text{VB}} = C_1' \psi_{\text{covalent}} + C_2' \psi_{\text{ionic}} \quad (2.4.15)$$

$$\text{where } \psi_{\text{ionic}} = C_1'' \psi_A(1)\psi_A(2) + C_2'' \psi_B(1)\psi_B(2) \quad (2.4.16)$$

## 2.5 LCAO-MO TREATMENT OF $\text{H}_2^+$

### Expression of Molecular Orbital

The hydrogen molecule ion which contains two protons and one electron is the simplest molecule to be treated by LCAO-MO method. The lowest energy atomic orbital of the hydrogen atom is the 1s orbital. It is expected that the linear combination of 1s orbitals will yield molecular orbital of the lowest energy. Referring to the two hydrogen atoms of  $\text{H}_2^+$  as A and B, we may write the trial function in the LCAO-MO framework as

$$\psi_{\text{MO}} = C_1 \psi_{1s(A)} + C_2 \psi_{1s(B)} \quad (2.5.1)$$

The Schrödinger equation is

$$H_{\text{op}} \psi_{\text{MO}} = E \psi_{\text{MO}} \quad (2.5.2)$$

### Expression of Schrödinger Equation

where  $H_{\text{op}}$ , the Hamiltonian operator, is given by

$$H_{\text{op}} = -\frac{\hbar^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{(4\pi\epsilon_0)r_A} - \frac{e^2}{(4\pi\epsilon_0)r_B} + \frac{e^2}{(4\pi\epsilon_0)R} \quad (2.5.3)$$

The symbols  $r_A$ ,  $r_B$  and  $R$  represent distances as shown in Fig. 2.5.1.

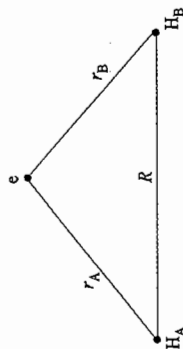


Fig. 2.5.1 The distances  $r_A$ ,  $r_B$  and  $R$  in the  $\text{H}_2^+$  ion

### Expectation Value of Energy

The energy  $E$  can be calculated by the expression

$$E = \frac{\langle \psi_{\text{MO}} | H_{\text{op}} | \psi_{\text{MO}} \rangle}{\langle \psi_{\text{MO}} | \psi_{\text{MO}} \rangle} \quad (2.5.4)$$

Substituting the expression of  $\psi_{\text{MO}}$  from Eq. (2.5.1), we get

$$E = \frac{\langle (C_1 \psi_{1s(A)} + C_2 \psi_{1s(B)}) | H_{\text{op}} | (C_1 \psi_{1s(A)} + C_2 \psi_{1s(B)}) \rangle}{\langle (C_1 \psi_{1s(A)} + C_2 \psi_{1s(B)}) | (C_1 \psi_{1s(A)} + C_2 \psi_{1s(B)}) \rangle} \\ = \frac{C_1^2 \langle \psi_{1s(A)} | H_{\text{op}} | \psi_{1s(A)} \rangle + C_2^2 \langle \psi_{1s(B)} | H_{\text{op}} | \psi_{1s(B)} \rangle + C_1 C_2 \langle \psi_{1s(B)} | H_{\text{op}} | \psi_{1s(A)} \rangle + C_1 C_2 \langle \psi_{1s(A)} | H_{\text{op}} | \psi_{1s(B)} \rangle}{C_1^2 \langle \psi_{1s(A)} | \psi_{1s(A)} \rangle + C_2^2 \langle \psi_{1s(B)} | \psi_{1s(B)} \rangle + 2 C_1 C_2 \langle \psi_{1s(A)} | \psi_{1s(B)} \rangle} \quad (2.5.5)$$

The Hamiltonian operator belongs to the class of Hermitian operator for which

$$\langle \psi_{1s(A)} | H_{\text{op}} | \psi_{1s(B)} \rangle = \langle \psi_{1s(B)} | H_{\text{op}} | \psi_{1s(A)} \rangle \quad (2.5.6)$$

If the atomic orbitals are normalized, we will have

$$\langle \psi_{1s(A)} | \psi_{1s(A)} \rangle = \langle \psi_{1s(B)} | \psi_{1s(B)} \rangle = 1 \quad (2.5.7)$$

With Eqs (2.5.6) and (2.5.7), Eq. (2.5.5) becomes

$$E = \frac{C_1^2 \langle \psi_{1s(A)} | H_{\text{op}} | \psi_{1s(A)} \rangle + C_2^2 \langle \psi_{1s(B)} | H_{\text{op}} | \psi_{1s(B)} \rangle + 2 C_1 C_2 \langle \psi_{1s(A)} | H_{\text{op}} | \psi_{1s(B)} \rangle}{C_1^2 + C_2^2 + 2 C_1 C_2 \langle \psi_{1s(A)} | \psi_{1s(B)} \rangle} \quad (2.5.8)$$

Following the notations

$$\langle \psi_{1s(A)} | H_{\text{op}} | \psi_{1s(A)} \rangle = \alpha_A$$

$$\langle \psi_{1s(B)} | H_{\text{op}} | \psi_{1s(B)} \rangle = \alpha_B$$

$$\langle \psi_{1s(A)} | H_{\text{op}} | \psi_{1s(B)} \rangle = \beta_{AB}$$

$$\text{and } \langle \psi_{1s(A)} | \psi_{1s(B)} \rangle = S_{AB}$$

We can write Eq. (2.5.8) as

$$E = \frac{C_1^2 \alpha_A + C_2^2 \alpha_B + 2C_1 C_2 \beta_{AB}}{C_1^2 + C_2^2 + 2C_1 C_2 S_{AB}} \quad (2.5.9)$$

The integrals  $\alpha_A$  and  $\alpha_B$  are known as *Coulomb integrals*. Their values are close to  $E_{1s(A)}$  and  $E_{1s(B)}$  respectively, where  $E_{1s(A)}$  and  $E_{1s(B)}$  represent respectively the energy of an electron in  $\psi_{1s(A)}$  and  $\psi_{1s(B)}$  in the isolated atoms.

The integral  $\beta_{AB}$  is known as *resonance integral*, whose value is a measure of the exchange of an electron from one atom to another. It always has a negative value.

The integral  $S_{AB}$  is known as *overlap integral*, and is a measure of the extent of overlapping of the two atomic orbitals.

The coefficients  $C_1$  and  $C_2$  in Eq. (2.5.9) are optimized by the variation method. To make the energy minimum, we set

$$\frac{\partial E}{\partial C_1} = 0 \quad \text{and} \quad \frac{\partial E}{\partial C_2} = 0$$

To determine  $\partial E / \partial C_1$ , we may write Eq. (2.5.9) as

$$E(C_1^2 + C_2^2 + 2C_1 C_2 S_{AB}) = C_1^2 \alpha_A + C_2^2 \alpha_B + 2C_1 C_2 \beta_{AB}$$

and then differentiate it with respect to  $C_1$ . Thus, we have

$$E(2C_1 + 2C_2 S_{AB}) + (C_1^2 + C_2^2 + 2C_1 C_2 S_{AB})(\partial E / \partial C_1) = 2C_1 \alpha_A + 2C_2 \beta_{AB}$$

$$\text{or} \quad \left( \frac{\partial E}{\partial C_1} \right) = \frac{2C_1 \alpha_A + 2C_2 \beta_{AB} - 2E(C_1 + C_2 S_{AB})}{C_1^2 + C_2^2 + 2C_1 C_2 S_{AB}}$$

On setting this expression to zero, we get

$$C_1 \alpha_A + C_2 \beta_{AB} - E(C_1 + C_2 S_{AB}) = 0 \quad (2.5.10)$$

Similarly, evaluating  $\partial E / \partial C_2$ , we get

$$C_1 \beta_{AB} + C_2 \alpha_B - E(C_1 S_{AB} + C_2) = 0 \quad (2.5.11)$$

Equations (2.5.10) and (2.5.11) may be written as

$$C_1(\alpha_A - E) + C_2(\beta_{AB} - ES_{AB}) = 0 \quad (2.5.12a)$$

$$C_1(\beta_{AB} - ES_{AB}) + C_2(\alpha_B - E) = 0 \quad (2.5.12b)$$

or, in the matrix form, we have

$$\begin{vmatrix} \alpha_A - E & \beta_{AB} - ES_{AB} \\ \beta_{AB} - ES_{AB} & \alpha_B - E \end{vmatrix} \begin{vmatrix} C_1 \\ C_2 \end{vmatrix} = 0 \quad (2.5.13)$$

In order to have nontrivial solutions, we must set the determinant of the coefficient equal to zero, i.e.

$$\begin{vmatrix} \alpha_A - E & \beta_{AB} - ES_{AB} \\ \beta_{AB} - ES_{AB} & \alpha_B - E \end{vmatrix} = 0 \quad (2.5.14)$$

Equations 2.5.12 are known as *secular equations* and the determinant of Eq. (2.5.14) is known as the *secular determinant*.

Expanding the determinant of Eq. (2.5.14), we get

$$(\alpha_A - E)(\alpha_B - E) - (\beta_{AB} - ES_{AB})^2 = 0 \quad (2.5.15)$$

Equation (2.5.15) is quadratic expression in  $E$  and, in principle, can be solved for the two roots of  $E$ . These roots are then substituted in Eqs (2.5.12) to get the expressions for  $C_1$  and  $C_2$  for each root separately. The numerical values of  $C_1$  and  $C_2$  can be determined by making use of the normalization condition of molecular orbital. Thus, we have determined the coefficients  $C_1$  and  $C_2$  of the two molecular orbitals (Eq. 2.5.1) and the energy associated with each of these molecular orbitals. In general, we will get as many molecular orbitals as the number of atomic orbitals of which we have taken the linear combination.

For the hydrogen molecule ion, the problem is very much simplified as the atomic orbitals which we have mixed are of identical nature. It follows that

$$\alpha_A = \alpha_B = \alpha \quad (2.5.16)$$

and thus Eq. (2.5.15) becomes

$$(\alpha - E)^2 - (\beta_{AB} - ES_{AB})^2 = 0$$

$$\text{or} \quad \alpha - E = \pm (\beta_{AB} - ES_{AB})$$

Hence the two roots are

$$E_+ = \frac{\alpha + \beta_{AB}}{1 + S_{AB}} \quad (2.5.17a)$$

$$E_- = \frac{\alpha - \beta_{AB}}{1 - S_{AB}} \quad (2.5.17b)$$

These energies on substituting in Eqs (2.5.12) give

$$C_1 = \pm C_2 \quad (2.5.18)$$

Hence, we have

$$\psi_{+MO} = C_+(\psi_{1s(A)} + \psi_{1s(B)}); \quad E_+ = \frac{\alpha + \beta_{AB}}{1 + S_{AB}} \quad (2.5.19a)$$

$$\psi_{-MO} = C_-(\psi_{1s(A)} - \psi_{1s(B)}); \quad E_- = \frac{\alpha - \beta_{AB}}{1 - S_{AB}} \quad (2.5.19b)$$

where the constants  $C_+$  and  $C_-$  may be evaluated by applying the criterion that the molecular orbitals are normalized. Thus, we have

$$\langle \psi_{+MO} | \psi_{+MO} \rangle = 1$$

$$\text{i.e.} \quad C_+^2 \{ \langle \psi_{1s(A)} | \psi_{1s(A)} \rangle + \langle \psi_{1s(B)} | \psi_{1s(B)} \rangle + 2 \langle \psi_{1s(A)} | \psi_{1s(B)} \rangle \} = 1$$

$$\text{or} \quad C_+^2 (1 + 1 + 2S_{AB}) = 1$$

$$\text{Thus } C_+ = \frac{1}{\sqrt{2(1+S_{AB})}} \quad (2.5.20a)$$

Similarly, we can determine  $C_-$ , for which, we have

$$C_- = \frac{1}{\sqrt{2(1-S_{AB})}} \quad (2.5.20b)$$

### Analysis of the Term $\alpha_A$

The term  $\alpha_A$  is given by

$$\alpha_A = \langle \psi_{1s(A)} | H_{op} | \psi_{1s(A)} \rangle$$

$$\text{Since } H_{op} = -\frac{h^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{(4\pi\epsilon_0)r_A} - \frac{e^2}{(4\pi\epsilon_0)r_B} + \frac{e^2}{(4\pi\epsilon_0)R}$$

$$\begin{aligned} \text{we have } \alpha_A &= \langle \psi_{1s(A)} | -\frac{h^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{(4\pi\epsilon_0)r_A} - \frac{e^2}{(4\pi\epsilon_0)r_B} + \frac{e^2}{(4\pi\epsilon_0)R} | \psi_{1s(A)} \rangle \\ &= \langle \psi_{1s(A)} | -\frac{h^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{(4\pi\epsilon_0)r_A} | \psi_{1s(A)} \rangle \\ &\quad + \langle \psi_{1s(A)} | -\frac{e^2}{(4\pi\epsilon_0)r_B} | \psi_{1s(A)} \rangle + \langle \psi_{1s(A)} | \frac{e^2}{(4\pi\epsilon_0)R} | \psi_{1s(A)} \rangle \quad (2.5.21) \end{aligned}$$

The first term is equal to the energy of 1s orbital of an isolated hydrogen atom. Since the internuclear distance  $R$  is held constant (Born-Oppenheimer approximation), the third term is simply equal to  $e^2/(4\pi\epsilon_0)R$ . The second term represents the electrostatic attraction between proton B and an electron in a 1s orbital centred on proton A and is known as *Coulomb integral*. Since the latter represents an attractive term, it has a negative value. Writing the Coulomb integral as  $J$ , Eq. (2.5.21) may be written as

$$\alpha_A = E_{1s(H)} + J + \frac{e^2}{(4\pi\epsilon_0)R} \quad (2.5.22)$$

The term  $\beta_{AB}$  is given by

$$\begin{aligned} \beta_{AB} &= \langle \psi_{1s(A)} | H_{op} | \psi_{1s(B)} \rangle \\ &= \langle \psi_{1s(A)} | -\frac{h^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{(4\pi\epsilon_0)r_B} | \psi_{1s(B)} \rangle \\ &\quad + \langle \psi_{1s(A)} | -\frac{e^2}{(4\pi\epsilon_0)r_A} | \psi_{1s(B)} \rangle + \langle \psi_{1s(A)} | \frac{e^2}{(4\pi\epsilon_0)R} | \psi_{1s(B)} \rangle \\ &= E_{1s(H)} S_{AB} + K + \left( \frac{e^2}{(4\pi\epsilon_0)R} \right) S_{AB} \quad (2.5.23) \end{aligned}$$

### Analysis of the Term $\beta_{AB}$

where  $K$  is given by

$$K = \langle \psi_{1s(A)} | -\frac{e^2}{(4\pi\epsilon_0)r_A} | \psi_{1s(B)} \rangle$$

and is known as *exchange integral* as roughly speaking it represents some sort of exchange of electron between protons A and B and has a negative value. In general, the value of  $K$  depends on the physical overlap of the orbitals in question. Its magnitude also depends on the relative energies of the orbitals involved; the value is maximum when the two orbitals have the same energy, and it decreases as the difference of energies increases.

With Eqs (2.5.22) and (2.5.23), the energies  $E_+$  and  $E_-$  as given by Eqs (2.5.19) become

$$E_+ = \frac{\alpha + \beta_{AB}}{1 + S_{AB}} = E_{1s(H)} + \frac{e^2}{(4\pi\epsilon_0)R} + \frac{J + K}{1 + S_{AB}} \quad (2.5.24a)$$

$$E_- = \frac{\alpha - \beta_{AB}}{1 - S_{AB}} = E_{1s(H)} + \frac{e^2}{(4\pi\epsilon_0)R} + \frac{J - K}{1 - S_{AB}} \quad (2.5.24b)$$

The hydrogen 1s orbital is given by the expression

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} \exp(-r/a_0)$$

In atomic units<sup>†</sup>, we have

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \exp(-r)$$

Substituting this in the expressions of  $J$ ,  $K$  and  $S_{AB}$  and then evaluating the integrals, we get

$$J = \langle \psi_{1s(A)} | -\frac{e^2}{(4\pi\epsilon_0)r_B} | \psi_{1s(A)} \rangle = -\frac{1}{R} \{1 - (1 + R) \exp(-2R)\} \quad (2.5.25)$$

$$K = \langle \psi_{1s(A)} | -\frac{e^2}{(4\pi\epsilon_0)r_A} | \psi_{1s(B)} \rangle = -(1 + R) \exp(-R) \quad (2.5.26)$$

$$S_{AB} = \langle \psi_{1s(A)} | \psi_{1s(B)} \rangle = \left( 1 + R + \frac{R^2}{3} \right) \exp(-R) \quad (2.5.27)$$

where  $R$  is expressed in atomic units.<sup>††</sup>

<sup>†</sup> In atomic units, the energies are reported in *hartree* and distance in *bohr*. These quantities are defined as follows.

$$1 \text{ bohr} \approx a_0 = 52 \text{ pm}$$

$$1 \text{ hartree} = \frac{e^2}{(4\pi\epsilon_0)a_0} = 27.112 \text{ eV} = 2.617 \text{ MJ mol}^{-1}$$

See also Annexure VII at the end of Chapter 1.

<sup>††</sup> See Annexure II for the evaluation of integrals  $J$ ,  $K$  and  $S$ .



### Comparison of Energies $E_+$ and $E_-$

Comparison of energies  $E_+$  and  $E_-$  may be made by making use of either Eqs (2.5.19) or Eqs (2.5.24). For simplicity, we may assume,  $S_{AB} = 0$ . From Eqs (2.5.19), we have

$$E_+ = \alpha + \beta_{AB}$$

$$E_- = \alpha - \beta_{AB}$$

Since both  $\alpha$  and  $\beta_{AB}$  are negative, it is obvious that

$$E_+ < E_- \quad (2.5.28)$$

that is, the molecular orbital  $\psi_{+MO}$  has a lower energy than  $\psi_{-MO}$ . On comparing  $E_+$  and  $E_-$ , we find that

$$E_+ < \alpha \quad (2.5.29a)$$

$$E_- > \alpha \quad (2.5.29b)$$

The above analysis is shown schematically in Fig. 2.5.2.

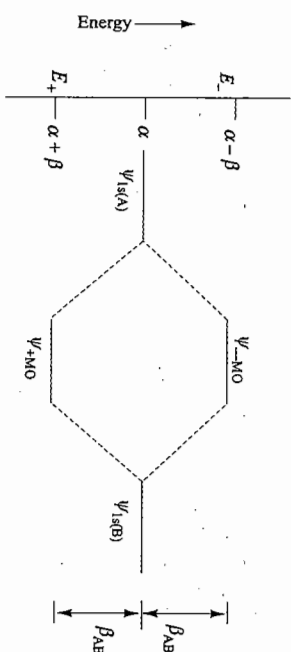


Fig. 2.5.2 Display of  $E_+$  and  $E_-$

Even if we include the overlap integral  $S_{AB}$ , the pattern shown in Fig. 2.5.2 is maintained, but the deviation of energies of molecular orbitals from that of 1s atomic orbital is uneven.

Coming to Eqs (2.5.24), the expressions after ignoring  $S_{AB}$  are

$$E_+ = E_{1s(H)} + \frac{e^2}{(4\pi\epsilon_0)R} + (J + K)$$

$$E_- = E_{1s(H)} + \frac{e^2}{(4\pi\epsilon_0)R} + (J - K)$$

At larger internuclear distances, the terms  $J$  and  $K$  show the following characteristics:

$J$  varies as  $1/R$

$K$  varies inverse exponentially with  $R$ .

Since the term  $J$  has a form of  $-1/R$ , it is largely cancelled by the nuclear repulsion term  $1/R$ . Now since  $K$  has a negative value, we may conclude that

$$E_+ < E_{1s(H)}$$

$$E_- > E_{1s(H)}$$

the conclusions which are identical to those of Eqs (2.5.29).

### Bonding and Antibonding Orbitals

#### Potential Energy Curves for $H_2^+$

A molecular orbital whose energy is lesser than those of the isolated atomic orbitals is called a *bonding molecular orbital*. Placing the electron in this orbital decreases the energy of the system, and hence contributes towards the formation of a chemical bond. Conversely, if the energy of molecular orbital is larger than those of isolated atomic orbitals, it is known as *antibonding molecular orbital*. Placing the electron in this orbital contributes towards making the molecule less stable.

In  $H_2^+$ ,  $\psi_{+MO}$  is the bonding molecular orbital whereas  $\psi_{-MO}$  is the antibonding molecular orbital.

The potential energy curve depicts the variation of energy of a molecular orbital with the internuclear distance. For the orbitals  $\psi_{+MO}$  and  $\psi_{-MO}$ , the plots of  $E_+ - E_{1s(H)}$  versus  $R$  and  $E_- - E_{1s(H)}$  versus  $R$  are shown in Fig. 2.5.3.<sup>†</sup> The calculated bond energy (the maximum depth in the  $E_+$  curve) is about 60% of the correct value.

The potential energy of  $\psi_{+MO}$  contains a minimum which will correspond to a stable  $H_2^+$  molecule. The minimum occurs at 132 pm (known as *bond distance*) with the depth equal to 1.77 eV, i.e. 170.8 kJ mol<sup>-1</sup> (known as *bond energy*). The observed values are 106 pm and 2.79 eV, i.e. 269.2 kJ mol<sup>-1</sup>. The agreement between the calculated and observed values is not very satisfactory. The calculated values can be improved further by introducing additional parameters into the trial function, such as including additional atomic orbitals and treating  $Z$ , the nuclear charge, to be effective nuclear charge.

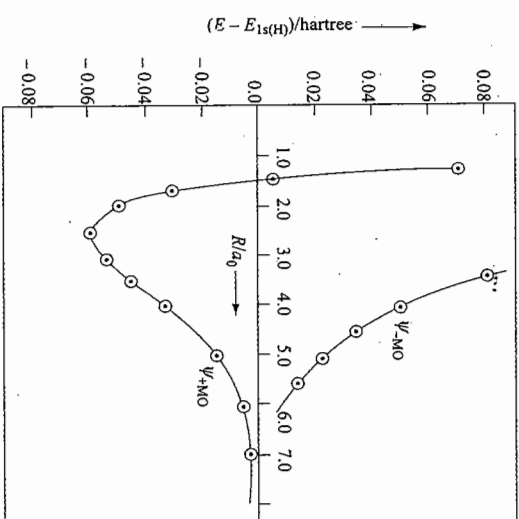


Fig. 2.5.3 Variation of energies of  $\psi_{+MO}$  and  $\psi_{-MO}$  with internuclear distance

The relative contribution of the various terms in Eqs (2.5.24) at the calculated bond distance are shown in Fig. 2.5.4. Note that the bond energy is small difference between large numbers.

<sup>†</sup> For the data, see Try Yourself Problem 2.28.



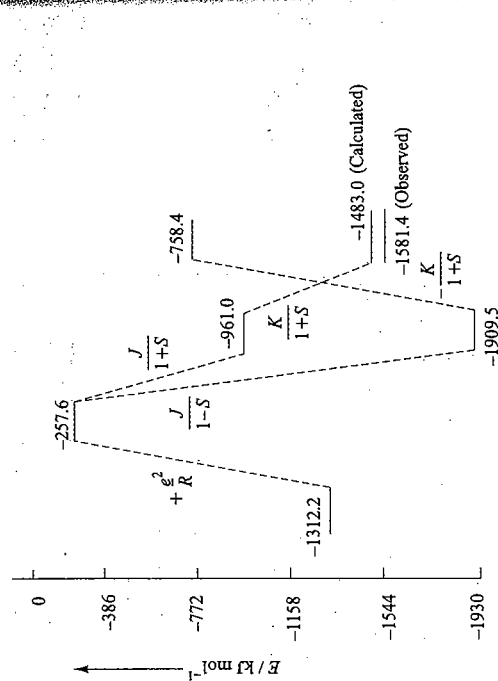


Fig. 2.5.4 Contributions of various terms in the energy of  $\psi_{+MO}$  and  $\psi_{-MO}$

### Graphical Representation of $\psi_{+MO}$ and $\psi_{-MO}^2$

The graphical representation of  $\psi_{+MO}$  and  $\psi_{-MO}$  can be drawn by simply taking the algebraic addition and subtraction of two atomic orbitals  $\psi_{1s(A)}$  and  $\psi_{1s(B)}$ . These are shown in Fig. 2.5.5.

The terms  $\psi_{+MO}$  and  $\psi_{-MO}^2$  represent the electron probability distributions associated with the molecular orbitals  $\psi_{+MO}$  and  $\psi_{-MO}$ , respectively.

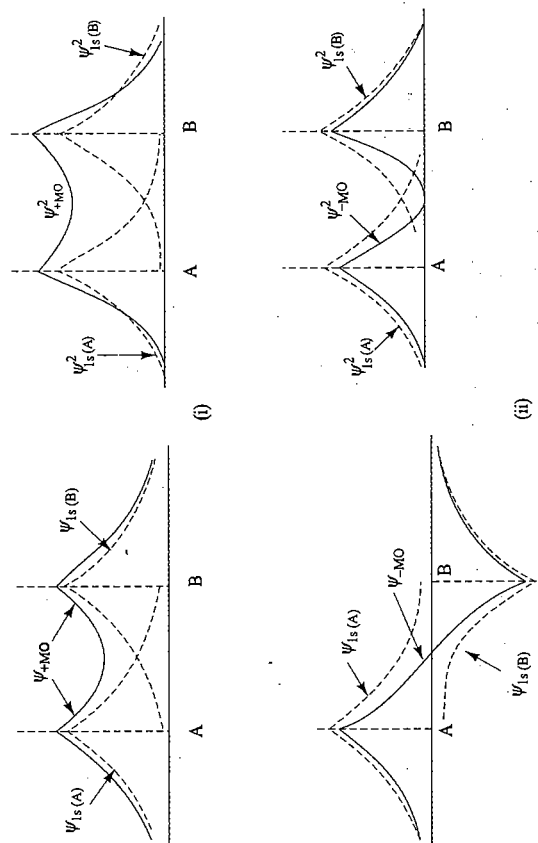


Fig. 2.5.5 Graphical representation of (i)  $\psi_{+MO}$  and  $\psi_{-MO}$  and (ii)  $\psi_{+MO}$  and  $\psi_{-MO}$

We have

$$\psi_{+MO}^2 = \frac{\psi_{1s(A)}^2 + \psi_{1s(B)}^2 + 2\psi_{1s(A)}\psi_{1s(B)}}{2 + 2S_{AB}} \quad (2.5.30)$$

$$\psi_{-MO}^2 = \frac{\psi_{1s(A)}^2 + \psi_{1s(B)}^2 - 2\psi_{1s(A)}\psi_{1s(B)}}{2 - 2S_{AB}} \quad (2.5.31)$$

In the region between the two nuclei, both  $\psi_{1s(A)}$  and  $\psi_{1s(B)}$  have appreciable values, and so does their product. In  $\psi_{+MO}^2$ , the term  $2\psi_{1s(A)}\psi_{1s(B)}$  which appears in the numerator has a positive sign indicating that the probability of finding the electron between the two nuclei is relatively high. The electrons in this region interact with both the nuclei and hence the electrostatic attraction has a large negative value. This attraction is larger than the nuclear repulsion. Thus, there is a release of energy (or lowering of interpotential energy) when an electron is placed in the bonding orbital.

The antibonding orbital has a zero value wherever  $\psi_{1s(A)}$  and  $\psi_{1s(B)}$  have the same value. This occurs at  $r = R/2$ . Thus, the molecular orbital  $\psi_{-MO}$  has a zero value in a plane which is perpendicular to and bisects the axis between the two nuclei. This plane is known as *nodal plane*. The value of  $\psi_{-MO}^2$  is also zero on the nodal plane. Thus, the probability of finding an electron on the nodal plane is zero and it is low in the region between the nuclei. In other words, the electron tends to avoid the region where it can interact with both nuclei. Hence, the electrostatic repulsion between the two nuclei is more than the net electrostatic attraction and thus there occurs an increase in potential energy when an electron is placed in the antibonding orbital. The representations of  $\psi_{+MO}^2$  and  $\psi_{-MO}^2$  are also shown in Fig. 2.5.5.

### Problem 2.5.1

(a) Making use of LCAO and zero-overlap approximations, derive the various molecular orbitals (involving only valence atomic orbitals) and the associated energies for  $H_3^{2+}$  molecule in the (i) linear, and (ii) equilateral triangle structures. Assume  $\beta_{ab} = \beta$  for the next nearest neighbours and  $\beta_{ab} = 0$  for all other exchange integrals.

(b) Justify the fact that the geometry of  $H_3$  is linear whereas that of  $H_3^+$  is an equilateral triangle.

(c) Assuming that the energies of molecular orbitals of  $H_3^{2+}$  are applicable to  $H_3^+$  and  $H_3$ , show that (i)  $H_3$  is stable with respect to  $3H$ , (ii)  $H_3^+$  is stable with respect to  $H^+$  and  $2H$ , and (iii)  $H_3^+$  is stable with respect to  $H^+$  and  $H_2$ .

(a) We write the molecular orbitals of  $H_3^{2+}$  as

$$\psi = C_1\psi_{1s(H_A)} + C_2\psi_{1s(H_B)} + C_3\psi_{1s(H_C)} \quad (1)$$

The energy of  $\psi$  is given by

$$E = \frac{\langle \psi | H_{op} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (2)$$

On substituting Eq. (1) in Eq. (2), we get

$$E = \frac{(C_1^2 + C_2^2 + C_3^2)\alpha + 2C_1C_2\beta_{ab} + 2C_1C_3\beta_{ac} + 2C_2C_3\beta_{bc}}{C_1^2 + C_2^2 + C_3^2 + 2C_1C_2S_{ab} + 2C_1C_3S_{ac} + 2C_2C_3S_{bc}} \quad (3)$$

where

$$\alpha = \langle \psi_{1s(H_a)} | H_{op} | \psi_{1s(H_b)} \rangle = \langle \psi_{1s(H_b)} | H_{op} | \psi_{1s(H_a)} \rangle = \langle \psi_{1s(H_a)} | H_{op} | \psi_{1s(H_b)} \rangle$$

$$\beta_{ij} = \langle \psi_{1s(H_i)} | H_{op} | \psi_{1s(H_j)} \rangle$$

$$S_{ij} = \langle \psi_{1s(H_i)} | \psi_{1s(H_j)} \rangle$$

(i) For linear structure, we will have  $\beta_{ac} = 0$  and  $S_{ab} = S_{bc} = S_{ac} = 0$ . With these, Eq. (3) becomes

$$E = \frac{(C_1^2 + C_2^2 + C_3^2)\alpha + 2(C_1C_2 + C_2C_3)\beta}{C_1^2 + C_2^2 + C_3^2}$$

Minimizing  $E$  with respect to  $C_1$ ,  $C_2$  and  $C_3$  (i.e., substituting  $\partial E/\partial C_1 = \partial E/\partial C_2 = \partial E/\partial C_3 = 0$ ), we get the three secular equations

$$C_1(\alpha - E) + C_2\beta = 0 \quad (4)$$

$$C_1\beta + C_2(\alpha - E) + C_3\beta = 0 \quad (5)$$

$$C_2\beta + C_3(\alpha - E) = 0 \quad (6)$$

Writing Eqs (4)–(6) in the determinant form, we get

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} \begin{vmatrix} C_1 \\ C_2 \\ C_3 \end{vmatrix} = 0$$

where  $x = (\alpha - E)/\beta$ . In order to get nontrivial roots, we write

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

$$\text{Thus } x(x^2 - 2) = 0$$

which gives  $x = -\sqrt{2}$ , 0 and  $\sqrt{2}$  as the three roots.

Substituting  $x = -\sqrt{2}$  in  $x = (\alpha - E)/\beta$ , we get

$$E = \alpha + \sqrt{2}\beta$$

Substituting the above expression in the secular equations, we get

$$C_1(-\sqrt{2}\beta) + C_2\beta = 0$$

$$C_1\beta + C_2(-\sqrt{2}\beta) + C_3\beta = 0$$

$$C_2\beta + C_3(-\sqrt{2}\beta) = 0$$

From the above equations, we find

$$C_1 = C_3 \quad \text{and} \quad C_2 = \sqrt{2}C_1$$

Substituting these in the normalization condition

$$C_1^2 + C_2^2 + C_3^2 = 1$$

we get  $C_1 = \frac{1}{2}$ ,  $C_2 = \frac{1}{\sqrt{2}}$  and  $C_3 = \frac{1}{2}$

Thus, the molecular orbital  $\psi_{1,lin}$  is given by

$$\psi_{1,lin} = \frac{1}{2} \psi_{1s(H_a)} + \frac{1}{\sqrt{2}} \psi_{1s(H_b)} + \frac{1}{2} \psi_{1s(H_c)}; \quad E_{1,lin} = \alpha + \sqrt{2}\beta \quad (7)$$

Proceeding similarly for other two roots, we get

$$\psi_{2,lin} = \frac{1}{\sqrt{2}} \psi_{1s(H_a)} - \frac{1}{\sqrt{2}} \psi_{1s(H_b)}; \quad E_{2,lin} = \alpha \quad (8)$$

(nonbonding)

$$\psi_{3,lin} = \frac{1}{2} \psi_{1s(H_a)} - \frac{1}{\sqrt{2}} \psi_{1s(H_b)} + \frac{1}{2} \psi_{1s(H_c)}; \quad E_{3,lin} = \alpha - \sqrt{2}\beta \quad (9)$$

(antibonding)

(ii) For equilateral triangle structure, we will have  $S_{ab} = S_{bc} = S_{ac} = 0$ . With these, Eq. (3) becomes

$$E = \frac{(C_1^2 + C_2^2 + C_3^2)\alpha + 2(C_1C_2 + C_2C_3 + C_1C_3)\beta}{C_1^2 + C_2^2 + C_3^2}$$

Minimizing  $E$  with respect to  $C_1$ ,  $C_2$  and  $C_3$ , we get

$$C_1(\alpha - E) + C_2\beta + C_3\beta = 0$$

$$C_1\beta + C_2(\alpha - E) + C_3\beta = 0$$

$$C_1\beta + C_2\beta + C_3(\alpha - E) = 0$$

which will give

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0$$

$$\text{or } (x-1)(x^2 + x - 2) = 0$$

The three roots are  $-2$ , 1 and 1.

Substituting  $x = -2$  in  $x = (\alpha - E)/\beta$ , we get

$$E = \alpha + 2\beta$$

Substituting the above expression in secular equations, we get

$$C_1(-2\beta) + C_2\beta + C_3\beta = 0$$

$$C_1\beta + C_2(-2\beta) + C_3\beta = 0$$

$$C_1\beta + C_2\beta + C_3(-2\beta) = 0$$

From the above equations, we find

$$C_1 = C_2 = C_3$$

which on substituting in the normalization condition give

$$C_1 = C_2 = C_3 = \frac{1}{\sqrt{3}}$$

Hence, we have

$$\psi_{1, \text{equil}} = \frac{1}{\sqrt{3}} \{ \psi_{1s(H_a)} + \psi_{1s(H_b)} + \psi_{1s(H_c)} \}; \quad E_{1, \text{equil}} = \alpha + 2\beta$$

(bonding)

For root  $x = 1$ , we find

$$E = \alpha - \beta$$

which on substituting in secular equations gives

$$C_1 + C_2 + C_3 = 0$$

Making use of the fact that the orbital next to the ground state will have one node, we may write

$$C_2 = 0 \quad \text{and} \quad C_1 = -C_3$$

From the normalization condition, we get

$$C_1 = \frac{1}{\sqrt{2}} \quad \text{and} \quad C_3 = -\frac{1}{\sqrt{2}}$$

$$\text{Hence } \psi_{2, \text{(or 3), equil}} = \frac{1}{\sqrt{2}} \{ \psi_{1s(H_a)} - \psi_{1s(H_c)} \}; \quad E_{2, \text{equil}} = \alpha - \beta$$

(antibonding)

(b) In equilateral triangle structure, one electron is present in an orbital which is antibonding with respect to atoms a and c (i.e.  $\psi_{2, \text{equil}}$ ). In order to get stable structure, the electron in this orbital will try to keep the atoms a and c far apart from each other. But in the equilateral triangle structure, these two atoms are close to each other. Hence it is an unstable structure. The molecule will tend to attain a geometry in which atoms a and c are far apart as in the case of linear structure. Hence, the linear structure is preferred over the equilateral triangle structure. In  $H_3^+$ , the electron is not present in the antibonding orbital. Consequently, the equilateral triangle is preferred. This is supported by the fact that  $E_{1, \text{equil}} < E_{1, \text{lin}}$ .

(c) (i)  $E(H_3) = 3\alpha + 2\sqrt{2}\beta$  and  $E(3H) = 3\alpha$ . Since  $E(H_3) < E(3H)$ , it follows that  $H_3$  is more stable than  $3H$ .

(ii)  $E(H_3^+) = 2\alpha + 2\sqrt{2}\beta$  and  $E(H^+) + E(2H) = 2\alpha$ . Since the former is less than the latter,  $H_3^+$  is more stable than  $H^+ + 2H$ .

(iii)  $E(H_3^+) = 2\alpha + 2\sqrt{2}\beta$  and  $E(H^+) + E(H_2) = 2\alpha + 2\beta$ . Since the former is less than the latter,  $H_3^+$  is more stable than  $H^+ + H_2$ .

## 2.6 LCAO-MO TREATMENT OF A HYDROGEN MOLECULE

The hydrogen molecule contains two protons and two electrons. The spinless Hamiltonian operator is given by

$$H_{\text{op}} = -\frac{\hbar^2}{8\pi^2 m} \nabla_1^2 - \frac{\hbar^2}{8\pi^2 m} \nabla_2^2 - \frac{e^2}{(4\pi\epsilon_0)r_{1a}} - \frac{e^2}{(4\pi\epsilon_0)r_{1b}} - \frac{e^2}{(4\pi\epsilon_0)r_{2a}} - \frac{e^2}{(4\pi\epsilon_0)r_{2b}} + \frac{e^2}{(4\pi\epsilon_0)r_{ab}} + \frac{e^2}{(4\pi\epsilon_0)r_{12}} \quad (2.6.1)$$

where the various distances are shown in Fig. 2.6.1.

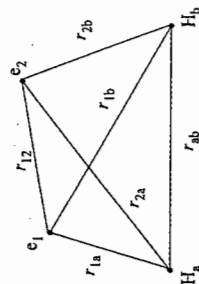


Fig. 2.6.1 Various distances between electrons and nuclei in hydrogen molecule

The two electrons will occupy the lowest bonding molecular orbital  $\psi_+$  with opposite spins. The total molecular wave function will include both the spatial and spin functions and will be given by

$$\psi_{\text{total}} = \psi_{\text{spatial}} \psi_{\text{spin}} \quad (2.6.2)$$

where  $\psi_{\text{spatial}} = \psi_+(1)\psi_+(2)$

$$\psi_{\text{spin}} = \frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2) - \alpha(2)\beta(1) \}$$

In the LCAO-MO framework,  $\psi_+$  will take the form of

$$\psi_+ = C_1 \psi_{1s(H_a)} + C_2 \psi_{1s(H_b)} \quad (2.6.3)$$

Since the two nuclei are identical, we will have

$$C_1 = C_2 = \frac{1}{\sqrt{2(1+S)}} \quad (2.6.4)$$

The energy of the system can be determined as usual by writing

$$E = \frac{\langle \psi_+(1) \psi_+(2) | H_{\text{op}} | \psi_+(1) \psi_+(2) \rangle}{\langle \psi_+(1) \psi_+(2) | \psi_+(1) \psi_+(2) \rangle} \quad (2.6.5)$$

From a quantitative point of view, the presence of two electrons in  $H_2$  produces mathematical complications because of electron-electron repulsion term in the Hamiltonian operator. Substitution of Eq. (2.6.3) in Eq. (2.6.5) produces a total energy minimum of  $-30.68 \text{ eV}$  ( $-2.96 \text{ MJ mol}^{-1}$ ) at the internuclear distance of 73 pm. The respective observed values are  $-31.95 \text{ eV}$  ( $-3.08 \text{ MJ mol}^{-1}$ ) and 74.1 pm. When the minimum is subtracted from the total energy of the two hydrogen atoms, we get the bond energy of the hydrogen molecule equal to 3.48 eV, i.e.  $335.78 \text{ kJ mol}^{-1}$  (calculated) and 4.75 eV, i.e.  $458.32 \text{ kJ mol}^{-1}$  (observed).

The bond energy of  $H_2$  molecule is larger than that of  $H_2^+$ . The bond distance of  $H_2$  molecule is smaller than that of  $H_2^+$ . These values may be interpreted in terms of more electron density in between the two nuclei.

## 2.7 VALENCE-BOND TREATMENT OF A HYDROGEN MOLECULE

The simplest wave function in valence-bond framework is given by

$$\psi = \psi_{1s(a)}(1) \psi_{1s(b)}(2) \quad (2.7.1)$$

The Hamiltonian operator of the hydrogen molecule (Eq. 2.6.1) may be written as

$$H_{op} = H_a + H_b + H' \quad (2.7.2)$$

$$\text{where } H_a = -\frac{h^2}{8\pi^2 m} \nabla_1^2 - \frac{e^2}{(4\pi\epsilon_0)r_{1a}} \equiv -\frac{h^2}{8\pi^2 m} \nabla_1^2 - \frac{e^2}{(4\pi\epsilon_0)r_{2a}}$$

$$H_b = -\frac{h^2}{8\pi^2 m} \nabla_2^2 - \frac{e^2}{(4\pi\epsilon_0)r_{2b}} \equiv -\frac{h^2}{8\pi^2 m} \nabla_2^2 - \frac{e^2}{(4\pi\epsilon_0)r_{1b}}$$

$$H' = -\frac{e^2}{(4\pi\epsilon_0)r_{1a}} - \frac{e^2}{(4\pi\epsilon_0)r_{1b}} + \frac{e^2}{(4\pi\epsilon_0)r_{12}} + \frac{e^2}{(4\pi\epsilon_0)r_{2a}} \\ \equiv \frac{e^2}{(4\pi\epsilon_0)r_{1a}} - \frac{e^2}{(4\pi\epsilon_0)r_{2b}} + \frac{e^2}{(4\pi\epsilon_0)r_{12}} + \frac{e^2}{(4\pi\epsilon_0)r_{2a}}$$

Assuming AOs are normalized, the energy of the wave function can be evaluated by using the expression

$$E = \langle \psi | H | \psi \rangle \quad (2.7.3)$$

On substituting Eq. (2.7.1) in Eq. (2.7.3), we get

$$E = \langle \psi_{1s(a)}(1) \psi_{1s(b)}(2) | H_a + H_b + H' | \psi_{1s(a)}(1) \psi_{1s(b)}(2) \rangle \\ = \langle \psi_{1s(a)}(1) | H_a | \psi_{1s(a)}(1) \rangle \langle \psi_{1s(b)}(2) | \psi_{1s(b)}(2) \rangle \\ + \langle \psi_{1s(b)}(2) | H_b | \psi_{1s(b)}(2) \rangle \langle \psi_{1s(a)}(1) | \psi_{1s(a)}(1) \rangle \\ + \langle \psi_{1s(a)}(1) \psi_{1s(b)}(2) | H' | \psi_{1s(a)}(1) \psi_{1s(b)}(2) \rangle \quad (2.7.4)$$

Since  $\psi_{1s(a)}$  and  $\psi_{1s(b)}$  are the normalized functions, Eq. (2.7.4) reduces to

$$E = E_{1s(a)} + E_{1s(b)} + Q = 2E_{1s(H)} + Q \quad (2.7.5)$$

$$\text{where } Q = \langle \psi_{1s(a)}(1) \psi_{1s(b)}(2) | H' | \psi_{1s(a)}(1) \psi_{1s(b)}(2) \rangle$$

On substituting the expression of  $H'$ , we will get

$$Q = -\langle \psi_{1s(a)}(1) | \frac{e^2}{(4\pi\epsilon_0)r_{1b}} | \psi_{1s(a)}(1) \rangle - \langle \psi_{1s(b)}(2) | \frac{e^2}{(4\pi\epsilon_0)r_{2a}} | \psi_{1s(b)}(2) \rangle \\ + \langle \psi_{1s(a)}(1) \psi_{1s(b)}(2) | \frac{e^2}{(4\pi\epsilon_0)r_{12}} | \psi_{1s(a)}(1) \psi_{1s(b)}(2) \rangle + \frac{e^2}{(4\pi\epsilon_0)r_{ab}}$$

The integral can be evaluated and is found to have a negative value.

The binding energy of the hydrogen molecule will be given by

$$E_{\text{binding}} = E(H_2) - 2E(H) = Q \quad (2.7.6)$$

When  $Q$  is evaluated at different values of  $r_{ab}$ , it is found to have a minimum of about 24 kJ mol<sup>-1</sup> at a distance of about 90 pm. The experimental values of binding energy and bond distance are 458 kJ mol<sup>-1</sup> and 74 pm, respectively. The agreement of calculated value of binding energy with the experimental value is only about 5 per cent.

### Heitler-London Wave Function

The above-mentioned poor agreement is due to the fact that it is not possible to label electrons since all electrons are indistinguishable from each other. Moreover, even if this labelling is possible, one would not be sure that electron 1 is associated with  $H_a$  and electron 2 with  $H_b$ . It might be possible that electron 1 is associated with  $H_b$  and electron 2 with  $H_a$ . Heitler and London incorporated this fact by writing the molecular wave function as

$$\psi_{\text{VB}} = C_1 \psi_{1s(a)}(1) \psi_{1s(b)}(2) + C_2 \psi_{1s(a)}(2) \psi_{1s(b)}(1) \quad (2.7.7)$$

We write Eq. (2.7.7) as

$$\psi_{\text{VB}} = C_1 \psi_1 + C_2 \psi_2 \quad (2.7.8)$$

$$\text{where } \psi_1 = \psi_{1s(a)}(1) \psi_{1s(b)}(2) \quad (2.7.9)$$

$$\text{and } \psi_2 = \psi_{1s(a)}(2) \psi_{1s(b)}(1) \quad (2.7.10)$$

The energy of  $H_2$  molecule is given by

$$E = \frac{\langle \psi_{\text{VB}} | H_{op} | \psi_{\text{VB}} \rangle}{\langle \psi_{\text{VB}} | \psi_{\text{VB}} \rangle} = \frac{\langle (C_1 \psi_1 + C_2 \psi_2) | H_{op} | (C_1 \psi_1 + C_2 \psi_2) \rangle}{\langle (C_1 \psi_1 + C_2 \psi_2) | (C_1 \psi_1 + C_2 \psi_2) \rangle} \\ = \frac{C_1^2 \langle \psi_1 | H_{op} | \psi_1 \rangle + C_2^2 \langle \psi_2 | H_{op} | \psi_2 \rangle + 2C_1 C_2 \langle \psi_1 | H_{op} | \psi_2 \rangle}{C_1^2 \langle \psi_1 | \psi_1 \rangle + C_2^2 \langle \psi_2 | \psi_2 \rangle + 2C_1 C_2 \langle \psi_1 | \psi_2 \rangle} \quad (2.7.11)$$

We have

$$\langle \psi_1 | \psi_1 \rangle = \langle \psi_{1s(a)}(1) \psi_{1s(b)}(2) | \psi_{1s(a)}(1) \psi_{1s(b)}(2) \rangle \\ = \langle \psi_{1s(a)}(1) | \psi_{1s(a)}(1) \rangle \langle \psi_{1s(b)}(2) | \psi_{1s(b)}(2) \rangle \\ = 1 \times 1 = 1$$

$$\begin{aligned}\langle \psi_2 | \psi_2 \rangle &= \langle \psi_{1s(H_A)}(2) | \psi_{1s(H_B)}(1) | \psi_{1s(H_A)}(2) | \psi_{1s(H_B)}(1) \rangle \\ &= \langle \psi_{1s(H_A)}(2) | \psi_{1s(H_A)}(2) \rangle \langle \psi_{1s(H_B)}(1) | \psi_{1s(H_B)}(1) \rangle \\ &= 1 \times 1 = 1\end{aligned}$$

$$\begin{aligned}\langle \psi_1 | \psi_2 \rangle &= \langle \psi_{1s(H_A)}(1) | \psi_{1s(H_B)}(2) | \psi_{1s(H_A)}(2) | \psi_{1s(H_B)}(1) \rangle \\ &= \langle \psi_{1s(H_A)}(1) | \psi_{1s(H_B)}(1) \rangle \langle \psi_{1s(H_B)}(2) | \psi_{1s(H_A)}(2) \rangle \\ &= S \times S = S^2\end{aligned}$$

where  $S$  is the overlap integral. Representing

$$\langle \psi_1 | H_{op} | \psi_1 \rangle = \alpha_1$$

$$\langle \psi_2 | H_{op} | \psi_2 \rangle = \alpha_2$$

$$\langle \psi_1 | H_{op} | \psi_2 \rangle = \beta_{12}$$

we can write Eq. (2.7.11) as

$$E = \frac{C_1^2 \alpha_1 + C_2^2 \alpha_2 + 2C_1 C_2 \beta_{12}}{C_1^2 + C_2^2 + 2C_1 C_2 S^2} \quad (2.7.12)$$

To minimize  $E$  with respect to  $C_1$  and  $C_2$ , we set

$$\frac{\partial E}{\partial C_1} = 0 \quad \text{and} \quad \frac{\partial E}{\partial C_2} = 0$$

To evaluate  $\partial E / \partial C_1$ , we write Eq. (2.7.12) as

$$E(C_1^2 + C_2^2 + 2C_1 C_2 S^2) = C_1^2 \alpha_1 + C_2^2 \alpha_2 + 2C_1 C_2 \beta_{12}$$

and differentiate it with respect to  $C_1$  to give

$$E(2C_1 + 2C_2 S^2) + \left( \frac{\partial E}{\partial C_1} \right) (C_1^2 + C_2^2 + 2C_1 C_2 S^2) = 2C_1 \alpha_1 + 2C_2 \beta_{12}$$

This gives

$$\frac{\partial E}{\partial C_1} = \frac{2C_1 \alpha_1 + 2C_2 \beta_{12} - E(2C_1 + 2C_2 S^2)}{C_1^2 + C_2^2 + 2C_1 C_2 S^2}$$

On setting the above expression equal to zero, we get

$$C_1 \alpha_1 + C_2 \beta_{12} - E(C_1 + C_2 S^2) = 0 \quad (2.7.13)$$

Similarly, evaluating  $\partial E / \partial C_2 = 0$ , we get

$$C_1 \beta_{12} + C_2 \alpha_2 - E(C_1 S^2 + C_2) = 0 \quad (2.7.14)$$

Equations (2.7.13) and (2.7.14) may be written as

$$C_1(\alpha_1 - E) + C_2(\beta_{12} - ES^2) = 0 \quad (2.7.15)$$

$$C_1(\beta_{12} - ES^2) + C_2(\alpha_2 - E) = 0 \quad (2.7.16)$$

These equations are known as *secular equations*. In the matrix form, we get

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} - ES^2 \\ \beta_{12} - ES^2 & \alpha_2 - E \end{vmatrix} \begin{vmatrix} C_1 \\ C_2 \end{vmatrix} = 0 \quad (2.7.17)$$

In order to have nontrivial solutions of secular equations, we set

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} - ES^2 \\ \beta_{12} - ES^2 & \alpha_2 - E \end{vmatrix} = 0 \quad (2.7.18)$$

This determinant is known as *secular determinant*. On opening the determinant, we get

$$(\alpha_1 - E)(\alpha_2 - E) - (\beta_{12} - ES^2)^2 = 0 \quad (2.7.19)$$

Equation (2.7.19) is quadratic in  $E$ , and provides two roots of  $E$ . These roots when substituted in the secular equations along with the normalization of the wave function  $\psi_{VB}$  provides the values of the coefficients  $C_1$  and  $C_2$ .

For hydrogen molecule, the functions  $\psi_1$  and  $\psi_2$  in  $\psi_{VB}$  involve the same type of atomic orbitals with the exception of allocation of electrons 1 and 2 to atomic orbitals. We may expect that

$$\alpha_1 = \alpha_2$$

Writing it as  $\alpha$  and  $\beta_{12}$  as  $\beta$ , Eq. (2.7.19) is simplified to

$$(\alpha - E)^2 - (\beta - ES^2)^2 = 0$$

this gives

$$\alpha - E = \pm (\beta - ES^2)$$

The two roots of  $E$  are

$$E_+ = \frac{\alpha + \beta}{1 + S^2} \quad \text{and} \quad E_- = \frac{\alpha - \beta}{1 - S^2} \quad (2.7.20)$$

Substituting the expression of  $E_+$  in Eq. (2.7.15), we get

$$C_1 \left( \alpha - \frac{\alpha + \beta}{1 + S^2} \right) + C_2 \left( \beta - \frac{\alpha + \beta}{1 + S^2} S^2 \right) = 0$$

On simplifying this expression, we get

$$C_1 = C_2 \quad (2.7.21)$$

Similarly, the substitution of the expression of  $E_-$  in Eq. (2.7.15), we get

$$C_1 = -C_2 \quad (2.7.22)$$

**Note:** The fact that  $C_1 = \pm C_2$  follows directly from the symmetry consideration of hydrogen molecule. Both the atoms will have identical charge densities and thus  $C_1^2 = C_2^2$ . From this it follows that  $C_1 = \pm C_2$ .

The constants  $C_1$  (or  $C_2$ ) may be evaluated by using the normalization expression of  $\psi_{\text{AB}}$ :

$$\int \psi_{\text{AB}}^2 d\tau = C_1^2 + C_2^2 + 2C_1 C_2 S^2 = 1$$

$$\text{For } C_1 = C_2, \text{ we get} \quad C_1 = \frac{1}{\sqrt{2(1+S^2)}} \quad (2.7.23)$$

$$\text{For } C_1 = -C_2, \text{ we get} \quad C_1 = \frac{1}{\sqrt{2(1-S^2)}} \quad (2.7.24)$$

We have

$$\begin{aligned} \alpha &= \langle \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) | H_{\text{op}} | \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) \rangle \\ &= \langle \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) | H_a + H_b + H' | \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) \rangle \\ &= \langle \psi_{\text{IsCH}_a}(1) | H_a | \psi_{\text{IsCH}_a}(1) \rangle \langle \psi_{\text{IsCH}_b}(2) | \psi_{\text{IsCH}_b}(2) \rangle \\ &\quad + \langle \psi_{\text{IsCH}_b}(2) | H_b | \psi_{\text{IsCH}_b}(2) \rangle \langle \psi_{\text{IsCH}_a}(1) | \psi_{\text{IsCH}_a}(1) \rangle \\ &\quad + \langle \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) | H' | \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) \rangle \\ &= E_{\text{IsCH}_a} \langle \psi_{\text{IsCH}_a}(1) | \psi_{\text{IsCH}_a}(1) \rangle \langle \psi_{\text{IsCH}_b}(2) | \psi_{\text{IsCH}_b}(2) \rangle \\ &\quad + E_{\text{IsCH}_b} \langle \psi_{\text{IsCH}_b}(2) | \psi_{\text{IsCH}_b}(2) \rangle \langle \psi_{\text{IsCH}_a}(1) | \psi_{\text{IsCH}_a}(1) \rangle \\ &\quad + \langle \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) | H' | \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) \rangle \\ &= E_{\text{IsCH}_a} + E_{\text{IsCH}_b} + Q \\ &= 2E_{\text{IsCH}} + Q \quad (2.7.25) \end{aligned}$$

**Analysis of  
Integral  $\beta$**

We have

$$\begin{aligned} \beta &= \langle \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) | H_a + H_b + H' | \psi_{\text{IsCH}_a}(2) \psi_{\text{IsCH}_b}(1) \rangle \\ &= \langle \psi_{\text{IsCH}_a}(1) | H_b | \psi_{\text{IsCH}_b}(1) \rangle \langle \psi_{\text{IsCH}_b}(2) | \psi_{\text{IsCH}_a}(2) \rangle \\ &\quad + \langle \psi_{\text{IsCH}_b}(2) | H_a | \psi_{\text{IsCH}_a}(2) \rangle \langle \psi_{\text{IsCH}_a}(1) | \psi_{\text{IsCH}_b}(1) \rangle \\ &\quad + \langle \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) | H' | \psi_{\text{IsCH}_a}(2) \psi_{\text{IsCH}_b}(1) \rangle \end{aligned}$$

**Expression of  
Energies**

Substituting Eqs (2.7.25) and (2.7.26) in Eq. (2.7.20), we get

$$\begin{aligned} &= E_{\text{IsCH}_a} \langle \psi_{\text{IsCH}_a}(1) | \psi_{\text{IsCH}_b}(1) \rangle \langle \psi_{\text{IsCH}_b}(2) | \psi_{\text{IsCH}_a}(2) \rangle \\ &\quad + E_{\text{IsCH}_a} \langle \psi_{\text{IsCH}_b}(2) | \psi_{\text{IsCH}_a}(2) \rangle \langle \psi_{\text{IsCH}_a}(1) | \psi_{\text{IsCH}_b}(1) \rangle \\ &\quad + \langle \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) | H' | \psi_{\text{IsCH}_a}(2) \psi_{\text{IsCH}_b}(1) \rangle \\ &= E_{\text{IsCH}_a} S^2 + E_{\text{IsCH}_a} S^2 + A \\ &= 2E_{\text{IsCH}} S^2 + A \quad (2.7.26) \end{aligned}$$

$$\begin{aligned} E_+ &= \frac{\alpha + \beta}{1 + S^2} = \frac{(2E_{\text{IsCH}} + Q) + (2E_{\text{IsCH}} S^2 + A)}{1 + S^2} \\ &= 2E_{\text{IsCH}} + \frac{Q + A}{1 + S^2} \quad (2.7.27) \end{aligned}$$

$$E_- = \frac{\alpha - \beta}{1 - S^2} = \frac{(2E_{\text{IsCH}} + Q) - (2E_{\text{IsCH}} S^2 + A)}{1 - S^2}$$

$$= 2E_{\text{IsCH}} + \frac{Q - A}{1 - S^2} \quad (2.7.28)$$

**Analysis of  
Integrals  $Q$  and  $A$**

On substitution the expression of  $H'$  in the expression of  $Q$  integral, we get

$$\begin{aligned} Q &= \langle \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) | -\frac{e^2}{(4\pi\epsilon_0)r_b} - \frac{e^2}{(4\pi\epsilon_0)r_a} + \frac{e^2}{(4\pi\epsilon_0)r_{ab}} | \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) \rangle \\ &\quad + \langle \psi_{\text{IsCH}_a}(1) | -\frac{e^2}{(4\pi\epsilon_0)r_b} | \psi_{\text{IsCH}_a}(1) \rangle \langle \psi_{\text{IsCH}_b}(2) | \psi_{\text{IsCH}_b}(2) \rangle \\ &\quad + \langle \psi_{\text{IsCH}_b}(2) | -\frac{e^2}{(4\pi\epsilon_0)r_a} | \psi_{\text{IsCH}_b}(2) \rangle \langle \psi_{\text{IsCH}_a}(1) | \psi_{\text{IsCH}_a}(1) \rangle \\ &\quad + \langle \psi_{\text{IsCH}_a}(1) | \psi_{\text{IsCH}_b}(2) | \frac{e^2}{(4\pi\epsilon_0)r_{ab}} | \psi_{\text{IsCH}_a}(1) \psi_{\text{IsCH}_b}(2) \rangle \\ &\quad + \frac{e^2}{(4\pi\epsilon_0)r_{ab}} \langle \psi_{\text{IsCH}_a}(1) | \psi_{\text{IsCH}_a}(1) \rangle \langle \psi_{\text{IsCH}_b}(2) | \psi_{\text{IsCH}_b}(2) \rangle \end{aligned}$$

$$\begin{aligned}
&= - \langle \psi_{1s(H_a)}(1) \left| \frac{e^2}{(4\pi\epsilon_0)r_{1b}} \right| \psi_{1s(H_a)}(1) \rangle - \langle \psi_{1s(H_b)}(2) \left| \frac{e^2}{(4\pi\epsilon_0)r_{2a}} \right| \psi_{1s(H_b)}(2) \rangle \\
&+ \langle \psi_{1s(H_a)}(1) \psi_{1s(H_b)}(2) \left| \frac{e^2}{(4\pi\epsilon_0)r_{12}} \right| \psi_{1s(H_a)}(1) \psi_{1s(H_b)}(2) \rangle + \frac{e^2}{(4\pi\epsilon_0)r_{ab}} \quad (2.7.29)
\end{aligned}$$

Similarly, the integral  $A$  can be analysed to give

$$\begin{aligned}
A = & -S \langle \psi_{1s(H_a)}(1) \left| \frac{e^2}{(4\pi\epsilon_0)r_{1b}} \right| \psi_{1s(H_b)}(1) \rangle - S \langle \psi_{1s(H_b)}(2) \left| \frac{e^2}{(4\pi\epsilon_0)r_{2a}} \right| \psi_{1s(H_a)}(2) \rangle \\
& + \langle \psi_{1s(H_a)}(1) \psi_{1s(H_b)}(2) \left| \frac{e^2}{(4\pi\epsilon_0)r_{12}} \right| \psi_{1s(H_a)}(2) \psi_{1s(H_b)}(1) \rangle + \frac{e^2 S^2}{(4\pi\epsilon_0)r_{ab}} \quad (2.7.30)
\end{aligned}$$

The integrals involved in Eq. (2.7.29) can be easily interpreted. For example, the first term represents the interaction of charge density of electron 1 around nucleus  $H_a$  with nucleus  $H_b$  via the Coulombic potential; the second term is the Coulombic energy of interaction of the charge density of electron 2 around  $H_b$  with nucleus  $H_a$ ; the third term is the mutual Coulombic interaction energy of the two electronic charge densities; and the fourth term is the nuclear-nuclear Coulombic interaction. Since each term in Eq. (2.7.29) can be interpreted as a classical Coulombic interaction,  $Q$  is referred to as the *Coulomb integral*. It is worth noticing that the integrals involved in Eq. (2.7.30) cannot be likewise interpreted. Its presence in the energy expressions is due to the form of the wave function (Eq. 2.7.7) which explicitly recognizes the indistinguishability of the two electrons. Consequently,  $A$  is a strictly quantum-mechanical quantity. Since  $A$  arises because of the exchange of electrons between the two nuclei, it is referred to as the *exchange integral*.

The integrals  $Q$  and  $A$  can be evaluated. Near the observed internuclear distance, both these integrals have negative values with  $A$  to be more negative than  $Q$ . With this fact, it follows that  $E_+ < E_-$ .

### Potential Energy Diagram

The energy of hydrogen molecule relative to two hydrogen atoms is given by

$$\Delta E_{\pm} = \frac{Q \pm A}{1 \pm S^2} \quad (2.7.31)$$

When  $\Delta E_{\pm}$  is plotted against the various values of  $r_{ab}$ , one gets the curves as shown in Fig. 2.7.1. It is obvious that  $\Delta E_+$  describes a stable chemical bond because the energy is less than that of the two isolated hydrogen atoms, whereas  $\Delta E_-$  describes a state that is unstable at all values of  $r_{ab}$ . The minimum of  $\Delta E_+$  versus  $r_{ab}$  curve occurs at 87 pm with  $|\Delta E_+| = 305 \text{ kJ mol}^{-1}$ . The observed values as stated above are 74.1 pm and  $458.32 \text{ kJ mol}^{-1}$ .

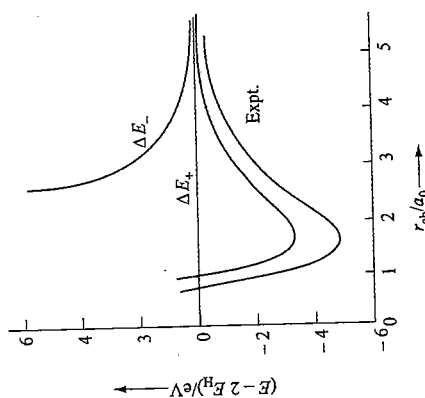


Fig. 2.7.1 Plot of  $\Delta E_{\pm}$  versus  $r_{ab}/a_0$

Thus, the agreement of calculated binding energy with the experimental energy is very much enhanced (about 66.6%). This is primarily due to the exchange integral.

The calculated binding energy can be improved further by including screening parameter (i.e. treating  $Z$  as the variable parameter instead of fixing it to unity) in the wave function. The value obtained is  $365 \text{ kJ mol}^{-1}$  at  $r_{\min} = 74.3 \text{ pm}$ . The agreement is thus enhanced to about 80 per cent. If, in addition to the above screening factor, the ionic structures are included,  $\Delta E_+$  and  $r_{\min}$  become  $388 \text{ kJ mol}^{-1}$  and  $74.9 \text{ pm}$ , respectively. The agreement in  $|\Delta E_+|$  becomes about 85 per cent.

## 2.8 COMPARISON BETWEEN MO AND VB TREATMENTS OF A HYDROGEN MOLECULE

In molecular orbital treatment of  $H_2$ , two electrons with opposite spins are assigned to the lowest molecular orbital  $\psi_+$ . Thus, the spatial wave function of  $H_2$  is

$$\begin{aligned}
\psi_{\text{spatial}} &= \psi_+(1)\psi_+(2) \\
&= \frac{1}{2(1+S)} \left\{ \psi_{1s(H_a)}(1) + \psi_{1s(H_b)}(1) \right\} \left\{ \psi_{1s(H_a)}(2) + \psi_{1s(H_b)}(2) \right\}
\end{aligned}$$

Opening out the above expression, we get

$$\begin{aligned}
\psi_{\text{spatial}} &= \frac{1}{2(1+S)} \left[ \psi_{1s(H_a)}(1)\psi_{1s(H_a)}(2) + \psi_{1s(H_a)}(1)\psi_{1s(H_b)}(2) \right. \\
&\quad \left. + \psi_{1s(H_b)}(1)\psi_{1s(H_a)}(2) + \psi_{1s(H_b)}(1)\psi_{1s(H_b)}(2) \right]
\end{aligned}$$

In the above expression, the various terms represent the structures as described below.

**First and fourth terms** The terms are  $\psi_{1s(H_a)}(1)\psi_{1s(H_a)}(2)$  and  $\psi_{1s(H_b)}(1)\psi_{1s(H_b)}(2)$ . These configurations assign both the electrons either to atom  $H_a$  or atom  $H_b$  and hence they represent ionic structures.

*Second and third terms* The terms are  $\psi_{\text{IsH}_a}(1)\psi_{\text{IsH}_b}(2)$  and  $\psi_{\text{IsH}_b}(1)\psi_{\text{IsH}_a}(2)$ . These configurations assign one electron to each of the atom and hence they represent covalent structures.

Since the coefficients of all the terms are identical, it follows that MO treatment gives equal weightage to the ionic and covalent structures. It is expected that the MO function will be poor at large internuclear separations since the dissociation products will be an equal mixture of ions and atom. In actual practice we get two hydrogen atoms. On the other hand, for very short internuclear distances one expects that there will also be some chance of finding both the electrons in the same atomic orbital. Thus, MO treatment does take into account this fact, but perhaps gives more weightage to this fact than what actually exists in the molecule.

The valence-bond treatment accounts for ionic structures by including the ionic structures to the Heitler-London wave function which represents the covalent structure. The amount of mixing is determined by the variation method which gives a value of 0.16 as the coefficient of ionic structure. The results of valence bond treatment has been modified by taking orbital exponent as the variable.

### Method of Configuration Interaction

The MO can be improved by the method of *configuration interaction*. In this, the wave function is taken as linear combination of functions arising from different electronic configurations. For hydrogen molecule, the following four spatial wave functions are possible:

$$\psi_1 = \psi_+(1)\psi_+(2)$$

$$\psi_2 = \psi_+(1)\psi_-(2) + \psi_-(1)\psi_+(2)$$

$$\psi_3 = \psi_-(1)\psi_-(2) - \psi_+(1)\psi_-(2)$$

$$\psi_4 = \psi_-(1)\psi_-(2)$$

In the wave function  $\psi_1$ , both the electrons are assigned to the ground state molecular orbital  $\psi_+$ , in  $\psi_2$  and  $\psi_3$ , one electron is assigned to  $\psi_+$  and the other to  $\psi_-$ , and in  $\psi_4$ , both the electrons are assigned to the antibonding molecular orbital  $\psi_-$ . Thus, in configuration interaction, we write the improved wave function as

$$\psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + C_4\psi_4 \quad (2.8.1)$$

where the coefficients are determined by the variation method.

Equation (2.8.1) can be simplified by considering the symmetry arguments. Only those configurations will mix which have the same symmetry with respect to the exchange of the two protons. Remembering that  $\psi_+$  and  $\psi_-$  are symmetrical and antisymmetrical wave functions, respectively, the symmetry nature of each of the above configurations can be worked out as follows.

$$\begin{array}{ll} \psi_1 = \psi_+(1)\psi_+(2); & \text{(symmetrical)} \\ \text{(sym)} & \text{(sym)} \\ \psi_2 = \psi_+(1)\psi_-(2) + \psi_-(1)\psi_+(2); & \text{(antisymmetrical)} \\ \text{(sym)} & \text{(antisym)} \end{array}$$

$$\begin{array}{llll} \psi_3 = \psi_+(1)\psi_-(2) - \psi_-(1)\psi_+(2); & \text{(antisymmetrical)} \\ \text{(sym)} & \text{(antisym)} & \text{(sym)} & \text{(antisym)} \\ \psi_4 = \psi_-(1)\psi_-(2); & & & \\ \text{(antisym)} & \text{(antisym)} & & \text{(symmetrical)} \end{array}$$

The functions  $\psi_1$  and  $\psi_4$  are symmetrical in nature whereas  $\psi_2$  and  $\psi_3$  are antisymmetrical. Hence, the configuration  $\psi_4$  will only mix up with the configuration  $\psi_1$ , thus, Eq. (2.8.1) reduces to<sup>†</sup>

$$\psi = C_1\psi_1 + C_4\psi_4 \quad (2.8.2)$$

Substituting the expressions of  $\psi_1$  and  $\psi_4$ , we get

$$\psi_1 = C_1\psi_+(1)\psi_+(2) + C_4\psi_-(1)\psi_-(2)$$

On substituting the LCAO expressions of  $\psi_+$  and  $\psi_-$ , we get

$$\begin{aligned} \psi = C_1 \{ & \psi_{\text{IsH}_a}(1) + \psi_{\text{IsH}_b}(1) \} \{ \psi_{\text{IsH}_a}(2) + \psi_{\text{IsH}_b}(2) \} \\ & + C_4 \{ \psi_{\text{IsH}_a}(1) - \psi_{\text{IsH}_b}(1) \} \{ \psi_{\text{IsH}_a}(2) - \psi_{\text{IsH}_b}(2) \} \end{aligned}$$

On opening the brackets and rearranging, we get

$$\psi = (C_1 - C_4) \psi_{\text{covalent}} + (C_1 + C_4) \psi_{\text{ionic}} \quad (2.8.3)$$

where  $\psi_{\text{covalent}} = \psi_{\text{IsH}_a}(1)\psi_{\text{IsH}_b}(2) + \psi_{\text{IsH}_b}(1)\psi_{\text{IsH}_a}(2)$

and  $\psi_{\text{ionic}} = \psi_{\text{IsH}_a}(1)\psi_{\text{IsH}_a}(2) + \psi_{\text{IsH}_b}(1)\psi_{\text{IsH}_b}(2)$

The interaction between the two configurations  $\psi_1$  and  $\psi_4$  in Eq. (2.8.2) will produce two refined molecular orbitals with the coefficient  $C_4$  having positive and negative values, respectively. From Eq. (2.8.3), it thus follows that the contributions of covalent and ionic structures in the refined molecular orbitals become uneven. In one of the refined molecular orbitals, the contribution of covalent structure will be larger than the ionic structure and it will be more stable than the stabler configuration  $\psi_1$ . In the second refined molecular orbital, the contribution of ionic structure will become more and it becomes less stable than the lesser stable configuration  $\psi_4$ .

From Eq. (2.8.3), it follows that molecular orbital theory with configuration interaction is exactly the same as valence-bond theory with ionic terms included. Both methods approach each other when more and more of covalent and ionic terms are included in VB theory and when more and more of excited-state configurations are included in the MO theory.

The MO theory is mathematically much simpler than the VB theory. The MO theory can be applied to large molecules easily with the help of electronic computers. By equating some of the cumbersome integrals to the experimental quantities and empirical parameters, the MO treatment to larger molecules has been very much simplified (see Section 2.16).

<sup>†</sup> In fact, when the elements of secular determinant for the function  $\psi$  are evaluated, the elements  $H_{12}$ ,  $H_{13}$ ,  $H_{24}$  and  $H_{34}$  will come out to be zero. This will lead to  $C_2 = C_3 = 0$  in one of the solutions of wave functions, i.e. it leads to wave function as given by Eq. (2.8.2).



## 2.9 MO TREATMENT OF HOMONUCLEAR DIATOMIC MOLECULES

### Shapes of Molecular Orbitals

In homonuclear diatomic molecules, we can form molecular orbitals by taking linear combinations of  $\psi_{1s(A)}$  and  $\psi_{1s(B)}$ ,  $\psi_{2s(A)}$  and  $\psi_{2s(B)}$ ,  $\psi_{2p_z(A)}$  and  $\psi_{2p_z(B)}$ ,  $\psi_{2p_x(A)}$  and  $\psi_{2p_x(B)}$ , and  $\psi_{2p_y(A)}$  and  $\psi_{2p_y(B)}$ , where  $z$ -axis is the internuclear axis. The combinations  $\psi_{2s(A)}$  and  $\psi_{2s(B)}$  (or  $\psi_{2p_z(A)}$  and  $\psi_{2p_z(B)}$ ) and  $\psi_{2p_x(A)}$  and  $\psi_{2p_x(B)}$  (or  $\psi_{2p_y(A)}$  and  $\psi_{2p_y(B)}$ ) do not produce any combination due to symmetry requirements. Each combination produces two molecular orbitals, bonding and antibonding (Table 2.9.1). Their shapes are shown in Fig. 2.9.1.

**Table 2.9.1 Molecular Orbitals of Homonuclear Diatomic Molecules formed from the Orbitals of Principal Quantum Number 2**

Molecular wave function	Bonding or antibonding	Designation
$N(\psi_{2s(A)} - \psi_{2s(B)})$	antibonding	$\sigma^*2s$ or $\sigma_u^*2s$
$N(\psi_{2s(A)} + \psi_{2s(B)})$	bonding	$\sigma 2s$ or $\sigma_g 2s$
$N(\psi_{2p_z(A)} + \psi_{2p_z(B)})$	antibonding	$\sigma^*2p$ or $\sigma_u^*2p$
$N(\psi_{2p_z(A)} - \psi_{2p_z(B)})$	bonding	$\sigma 2p$ or $\sigma_g 2p$
$N(\psi_{2p_x \text{ or } y(A)} - \psi_{2p_x \text{ or } y(B)})$	antibonding	$\pi^*2p$ or $\pi_g^*2p$
$N(\psi_{2p_x \text{ or } y(A)} + \psi_{2p_x \text{ or } y(B)})$	bonding	$\pi 2p$ or $\pi_u 2p$

The molecular orbitals formed from the orbitals of principal quantum number 3 can be similarly worked out.

### Designation of MO

The designation shown in the last column of Table 2.9.1 is based on the following facts.

(i) The value of component of the orbital angular momentum along the internuclear axis.

The component of the orbital angular momentum along the internuclear distance ( $z$ -axis) is  $\pm m_l h/2\pi$ , where  $m_l$  has integral values including zero, i.e.  $m_l = 0, 1, 2, 3, \dots$ . Except when  $m_l = 0$ , the orbitals are all doubly degenerate corresponding to the positive and negative angular momentum values along the  $z$ -axis. The designation of orbitals based on the value of  $m_l$  is given below:

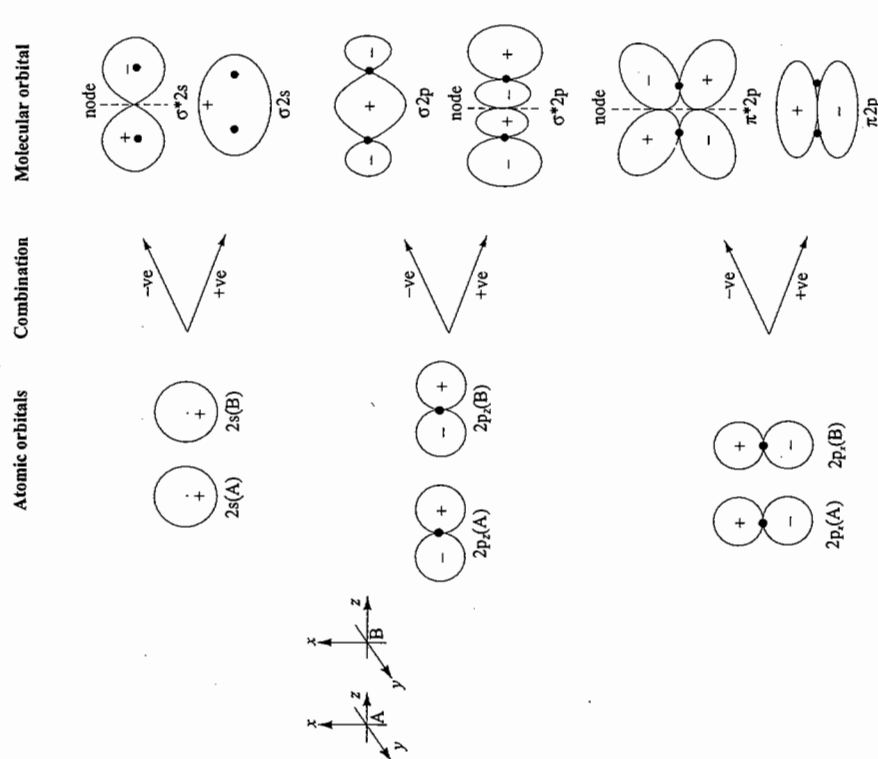
$m_l$	0	1	2	3	...
orbital type	$\sigma$	$\pi$	$\delta$	$\phi$	...

(ii) The atomic orbitals into which they separate at large distances.

The nature of orbitals to which a molecular orbital degenerates is shown by writing  $1s, 2s$ , etc., after the  $\sigma, \pi, \delta, \dots$ , symbols.

(iii) The bonding-antibonding character or the symmetry of the orbital with respect to its centre.

The above orbital designation is further labelled based on its bonding and antibonding character or on the symmetry of the orbitals with respect to its centre. In the former, antibonding orbitals are designated by placing an asterisk on the symbol listed above, the bonding orbitals do not carry any asterisk. Thus,  $\sigma, \pi$ , etc., are bonding orbitals and  $\sigma^*, \pi^*$ , etc., are antibonding orbitals. Alternatively, the symmetry of the orbitals with respect to its centre is shown by using the symbols  $g$  (*gerade*, the German word for even or symmetrical) and  $u$  (*ungerade*, the German word for odd or unsymmetrical) as the subscripts. From the contour diagrams of molecular orbitals shown in Fig. 2.9.1, it follows that the bonding orbitals  $\sigma 2s$  and  $\sigma 2p$ , and the antibonding orbital  $\pi^*2p$  are gerade in nature and thus are designated as  $\sigma_g 2s$ ,  $\sigma_g 2p$  and  $\pi_g^*2p$ , respectively. The antibonding orbitals  $\sigma^*2s$  and  $\sigma^*2p$  and the bonding orbital  $\pi 2p$  are ungerade in nature and thus are designated as  $\sigma_u^*2s$ ,  $\sigma_u^*2p$  and  $\pi_u 2p$ , respectively.



**Fig. 2.9.1 Formation of molecular orbitals from the linear combinations of two atomic orbitals**

### Relative Order of Energies of Molecular Orbitals without s-p Interaction

The relative order of energies of various molecular orbitals is required for writing down the electronic configuration of homonuclear diatomic molecules. The energy of a molecular orbital depends on the following two factors.

- (i) The type of atomic orbitals from which the molecular orbital is built up.
- (ii) The extent of overlap between the two involved orbitals.

Since the energy of 1s orbital is much lower than that of 2s orbital, it is obvious that  $\sigma 1s$  (or  $\sigma_g 1s$ ) and  $\sigma^* 1s$  (or  $\sigma_u 1s$ ) have energies lower than  $\sigma 2s$ . In turn, as 2s orbitals has lower energy than 2p, it is expected that  $\sigma 2s$  (or  $\sigma_g 2s$ ) lies below  $\sigma 2p$  (or  $\sigma_g 2p$ ). Since the end to end overlap between two 2s orbitals or two  $2p_z$  orbitals is larger than the sideways overlap between two  $2p_x$  or  $2p_y$  orbitals, it is expected that the separation between the bonding and antibonding  $\pi$  orbitals is lesser than the separation of those of  $\sigma$  orbitals.

From the above facts, we may draw the molecular orbital energy diagram as shown in Fig. 2.9.2.

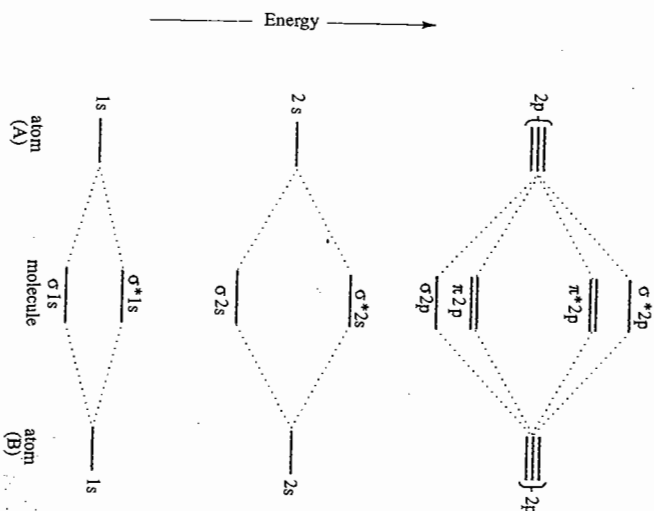


Fig. 2.9.2 Molecular orbital energy diagram

From Fig. 2.9.2, we may write

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p < \pi 2p < \pi^* 2p < \sigma^* 2p$$

### Order of Energy Levels with s-p Interaction

In terms of g and u representations, we have

$$\sigma_g 1s < \sigma_u 1s < \sigma_g 2s < \sigma_u 2s < \pi_u 2p < \pi_g 2p < \sigma_u 2p$$

In most cases, the orbitals 2s and 2p have energies close to each other. Because of this, the positive overlap between  $2s(A)$  and  $2p_z(B)$  or vice versa will also contribute to the formation of molecular orbitals. In other words, each of  $\sigma$  and  $\sigma^*$  molecular orbitals will be formed by mixing four atomic orbitals  $2s(A)$ ,  $2p_z(A)$ ,  $2s(B)$  and  $2p_z(B)$ . Such mixing will also modify the molecular orbital energy diagram. The resultant modifications may be shown conveniently by mixing  $\sigma 2s$  and  $\sigma 2p$ , and  $\sigma^* 2s$  and  $\sigma^* 2p$  as described by the following wave functions:

$$\psi_{+1} = C_1(\sigma 2s) + C_2(\sigma 2p) \quad (2.9.1)$$

$$\psi_{-2} = C_3(\sigma^* 2s) + C_4(\sigma^* 2p) \quad (2.9.2)$$

These interactions make  $\sigma 2s$  and  $\sigma^* 2s$  energetically more stable, and  $\sigma 2p$  and  $\sigma^* 2p$  less stable, i.e. the energies of  $\sigma 2s$  and  $\sigma^* 2s$  are lowered whereas those of  $\sigma 2p$  and  $\sigma^* 2p$  are raised. These energy modifications are shown in Fig. 2.9.3.

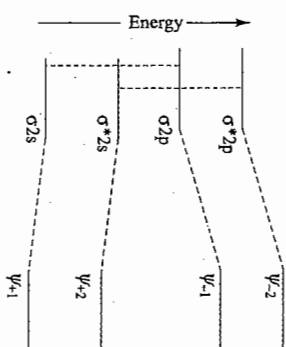


Fig. 2.9.3 Interaction between  $\sigma 2s$  and  $\sigma^* 2p$ , and  $\sigma^* 2s$  and  $\sigma^* 2p$  orbitals

For lighter molecules, the above interactions are important. Consequently, the energy of  $\sigma 2p$  orbital becomes larger than that of  $\pi 2p$  and thus the molecular orbital energy diagram is modified as shown in Fig. 2.9.4.

From Fig. 2.9.4, we may write

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p < \sigma 2p < \pi^* 2p < \sigma^* 2p$$

In terms of g and u representations, we have

$$\sigma_g 1s < \sigma_u 1s < \sigma_g 2s < \sigma_u 2s < \pi_u 2p < \sigma_g 2p < \pi_g 2p < \sigma_u 2p$$

This order holds for all the first row homonuclear diatomic molecules except  $O_2$  and  $F_2$ .

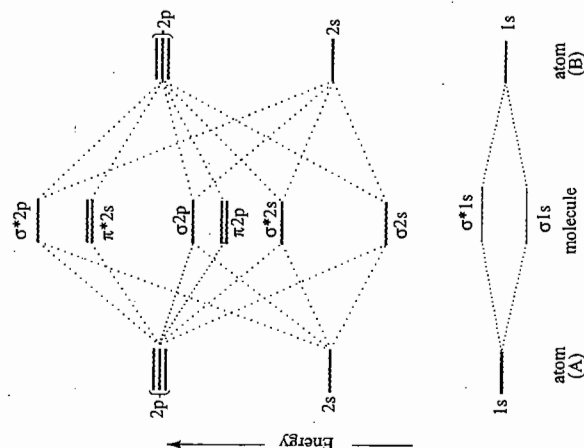


Fig. 2.9.4 Molecular orbital diagram where the interaction between 2s and 2p is observed

### Electronic Configurations of Homonuclear Diatomic Molecules

Following aufbau principle, Pauli exclusion principle and Hund's rule, we can write down electronic configurations of homonuclear diatomic molecules. Before we do so, it is worth considering a very important conclusion that *the electrons in the inner shells of atom play no effective part in molecular binding*. The justification for the above rule is given below.

Consider the configuration  $(\sigma 1s)^2(\sigma^* 1s)^2$  of some heavier homonuclear diatomic molecules (say, for example,  $C_2$ ). The charge distribution associated with the above configuration is

$$2(\sigma 1s)^2 + 2(\sigma^* 1s)^2$$

Substituting the expressions of  $\sigma 1s$  and  $\sigma^* 1s$ , we get

$$2 \times \left( \frac{\psi_{1s(A)} + \psi_{1s(B)}}{\sqrt{2(1+S)}} \right)^2 + 2 \times \left( \frac{\psi_{1s(A)} - \psi_{1s(B)}}{\sqrt{2(1-S)}} \right)^2$$

$$\text{or} \quad \frac{2}{1-S^2} \{ \psi_{1s(A)}^2 + \psi_{1s(B)}^2 - 2S\psi_{1s(A)}\psi_{1s(B)} \}$$

Now for  $C_2$ ,  $S \approx 10^{-5}$  for a normal C—C single bond. With this small value, the above expression reduces to

$$2(\psi_{1s(A)}^2 + \psi_{1s(B)}^2)$$

that is, it is simply equal to the sum of the electron densities of the  $1s(A)$  and  $1s(B)$  orbitals. This implies that in the formation of the diatomic molecules  $C_2$ ,

the electrons in the K-shells remain as they were in the isolated atoms. In other words, inner shells play no role in the molecular bonding. Thus, while writing the electronic configuration of any molecule heavier than hydrogen, we may write  $(\sigma 1s)^2(\sigma^* 1s)^2$  by KK, meaning that both the K-shells are fully occupied.

We may now write down the electronic configurations of homonuclear diatomic molecules  $H_2$  to  $F_2$  and some of their positive ions. These are shown in Table 2.9.2.

Table 2.9.2 The Lowest Electronic Configurations of the Homonuclear Diatomic Molecules

Molecule	Electronic configuration	Dissociation energy kJ mol <sup>-1</sup>	Net excess of bonding electrons	Bond order	Bond length/pm
$H_2$	$\sigma_g 1s$	255.7	1	0.5	106
$H_2^+$	$(\sigma_g 1s)^2$	432.3	2	1	74
$He_2^+$	$(\sigma_g 1s)^2(\sigma_u 1s)$	250.9 ± 48.2	1	0.5	108
$He_2$	$(\sigma_g 1s)^2(\sigma_u 1s)^2$	—	0	0	—
$Li_2$	KK $(\sigma_g 2s)^2$	110.0	2	1	267
$Be_2$	KK $(\sigma_g 2s)^2(\sigma_u 2s)^2$	—	0	0	—
$B_2$	$(Be_2)(\pi_u 2p)^2$	289.5 ± 48.2	2	1	159
$C_2$	$(Be_2)(\pi_u 2p)^4$	598.2	4	2	124
$N_2^+$	$(Be_2)(\pi_u 2p)^4(\sigma_g 2p)$	842.3	5	2.5	112
$N_2$	$(Be_2)(\pi_u 2p)^4(\sigma_g 2p)^2$	941.7	6	3	109
$O_2^+$	$(Be_2)(\sigma_g 2p)^3(\pi_u 2p)^4(\pi_g 2p)$	625.2	5	2.5	112
$O_2$	$(Be_2)(\sigma_g 2p)^3(\pi_u 2p)^4(\pi_g 2p)^2$	490.2	4	2	121
$F_2$	$(Be_2)(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^4$	154.4 ± 33.8	2	1	144
$Ne_2$	$(Be_2)(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^4(\pi_u 2p)^2$	—	0	0	—

### A Few

### Characteristics of Molecules

In general, we have

- The strength of a bond depends on the net excess of electrons in bonding orbitals over those of antibonding orbitals. Larger the bond strength, larger the dissociation energy of the molecule.
- The number of bonds or bond order in a molecule is one half of the net excess of bonding electrons.
- Addition of an electron in the bonding orbital makes the molecule more stable whereas that in the antibonding orbital makes it less stable.
- Paramagnetism in a substance is due to the presence of unpaired electrons in its molecules.

Keeping in mind the above characteristics, we may derive the following conclusions regarding some of the physical properties of diatomic molecules listed in Table 2.9.2.

1. The dissociation energy of  $H_2$  is almost twice that of  $H_2^+$ . This follows from the fact that  $H_2$  contains two bonding electrons in the  $\sigma_g$  orbitals whereas  $H_2^+$  contains only one. The decrease in bond length from  $H_2^+$  to  $H_2$  is also due to the above fact.
2. The dissociation energy of  $H_2^+$  is almost the same as that of  $He_2^+$ . The presence of one electron in  $\sigma_g$  orbitals in  $He_2^+$  under the effect of one electron in  $\sigma_g$  orbitals and thus  $He_2^+$  contains only one electron in  $\sigma_g$  orbitals.
3. The molecule  $He_2$  is not stable in the ground state as it contains equal number of electrons in the bonding  $\sigma_g$  orbitals and antibonding  $\sigma_u$  orbitals. Excited state of  $He_2$ , however, is observed. This is due to the promotion of electron from antibonding orbital to the bonding orbital.
4. The  $Be_2$  molecule likewise is not a stable molecule.
5.  $N_2^+$  is a paramagnetic substance as it contains one unpaired electron.
6.  $N_2$  has the maximum bond dissociation energy as it contains six net excess of bonding electrons. The bond between N and N is a triple bond.
7. In going from  $N_2$  to  $N_2^+$ , the bond energy weakens and bond length is increased. This follows from the fact that the electron removed is from the bonding orbital.
8.  $O_2$  molecule contains a double bond (one  $\sigma$  and the other  $\pi$ ). It is a paramagnetic substance, which is due to the presence of two unpaired electrons in the doubly degenerate  $\pi_g^* 2p$  orbitals.
9. In going from  $O_2$  to  $O_2^+$ , the bond dissociation energy is increased and the bond length is shortened. This follows from the fact that the electron removed is from the antibonding orbital.

### Problem 2.9.1

(a) Show that the wave functions  $\psi_{A1}$  and  $\psi_{B2}$  as described by Eqs 2.9.1 and 2.9.2, respectively, are equivalent to the molecular orbitals obtained by mixing the two hybrid orbitals centred on atoms A and B, respectively.

(b) Draw schematic contour diagrams of  $\psi_{A1}$  and  $\psi_{B2}$  starting from those of involved (i) molecular orbitals (i.e.  $\sigma 2s$ ,  $\sigma^* 2s$ , etc.) and (ii) hybrid orbitals (i.e.  $sp_1(A)$ ,  $sp_1(B)$ , etc.). Also infer whether the orbitals  $\psi_{A1}$  and  $\psi_{B2}$  will be more or less stable than its constituent orbitals.

Draw the correlation diagram for homonuclear diatomic molecules exhibiting s-p mixing.

(a) The expression of the wave function  $\psi_{A1}$  is

$$\psi_{A1} = C_1(\sigma 2s) + C_2(\sigma^* 2p)$$

The function  $\psi_{A1}$  will include more contribution from  $\sigma 2s$  (i.e.  $C_1 > C_2$ ) and also will be more stable than  $\sigma 2s$  orbital. On the other hand, the function  $\psi_{B1}$  will include more contribution from  $\sigma 2p$  (i.e.  $C_2 > C_1$ ) and will be less stable than this orbital.

Substituting the expressions of  $\sigma 2s$  and  $\sigma 2p$  (Table 2.9.1) in the wave function  $\psi_{A1}$ , we get

$$\begin{aligned}\psi_{A1} &= C_1 \{ N(\psi_{2s(A)} + \psi_{2s(B)}) \} + C_2 \{ N(\psi_{2p_z(A)} - \psi_{2p_z(B)}) \} \\ &= C_1' (\psi_{2s(A)} + \psi_{2s(B)}) + C_1' (\psi_{2s(B)} - \psi_{2p_z(B)}) \\ &= C_1' (\psi_{sp_1(A)} + \psi_{sp_1(B)})\end{aligned}$$

where  $C_1' = C_1 N$ ,  $C_2' = C_2 N$  and  $\lambda = C_2'/C_1'$ . Since  $C_1'$  is greater than  $C_2'$  for the wave function  $\psi_{A1}$ , the term  $\lambda$  will have a value less than one. Consequently, the hybrid orbitals  $sp_1(A)$  and  $sp_1(B)$  will include more weightage from the orbitals  $2s(A)$  and  $2s(B)$ , respectively.

For the function  $\psi_{B1}$ , we have

$$\begin{aligned}\psi_{B1} &= C_1 \{ N(\psi_{2s(A)} + \psi_{2s(B)}) \} - C_2 \{ N(\psi_{2p_z(A)} - \psi_{2p_z(B)}) \} \\ &= C_2' \{ \lambda \psi_{2s(A)} - \psi_{2p_z(A)} \} + C_2' \{ \lambda \psi_{2s(B)} + \psi_{2p_z(B)} \} \\ &= C_2' \{ \psi_{sp_2(A)} + \psi_{sp_2(B)} \}\end{aligned}$$

where  $C_2' = C_2 N$ ,  $C_1' = C_1 N$  and  $\lambda = C_1'/C_2'$ . Since  $C_2'$  is greater than  $C_1'$  for the wave function  $\psi_{B1}$ , the term  $\lambda$  will have a value less than one. Consequently, the hybrid orbitals  $sp_2(A)$  and  $sp_2(B)$  will include more weightage from the orbitals  $2p_z(A)$  and  $2p_z(B)$ , respectively.

For the function  $\psi_{A2}$ , we have

$$\begin{aligned}\psi_{A2} &= C_1 \{ N(\psi_{2s(A)} - \psi_{2s(B)}) \} + C_2 \{ N(\psi_{2p_z(A)} + \psi_{2p_z(B)}) \} \\ &= C_1' \{ \psi_{2s(A)} + \lambda \psi_{2p_z(A)} \} - C_1' \{ \psi_{2s(B)} - \lambda \psi_{2p_z(B)} \} \\ &= C_1' \{ \psi_{sp_1(A)} - \psi_{sp_1(B)} \}\end{aligned}$$

The function  $\psi_{A2}$  will include more contribution from  $\sigma^* 2s$  (i.e.  $C_1 > C_2$ ) and also will be more stable than  $\sigma^* 2s$  orbital.

For the function  $\psi_{B2}$ , we have

$$\begin{aligned}\psi_{B2} &= C_1 \{ N(\psi_{2s(A)} - \psi_{2s(B)}) \} - C_2 \{ N(\psi_{2p_z(A)} + \psi_{2p_z(B)}) \} \\ &= C_2' \{ \lambda \psi_{2s(A)} - \psi_{2p_z(A)} \} - C_2' \{ \lambda \psi_{2s(B)} + \psi_{2p_z(B)} \} \\ &= C_2' \{ \psi_{sp_2(A)} - \psi_{sp_2(B)} \}\end{aligned}$$

The function  $\psi_{B2}$  will include more contribution from  $\sigma^* 2p$  (i.e.  $C_2 > C_1$ ) and also will be less stable than  $\sigma^* 2p$  orbital.

(b) The following facts help constructing and understanding of the contour diagrams and correlation diagram depicted in Fig. 2.9.5 and Fig. 2.9.6, respectively.

(i) The energies of hybrid orbitals  $sp_1$  and  $sp_2$  will lie in between those of  $2s$  and  $2p_z$  orbitals. Since  $sp_1(A)$  and  $sp_1(B)$  include more weightage from the  $2s$  orbitals, their energies will be nearer to  $2s$  orbitals. On the other hand, the energies of  $sp_2(A)$  and  $sp_2(B)$  will be nearer to  $2p_z$  orbitals as they include more weightage from these orbitals.

(ii) The wave function  $\psi_{A1}$  and  $\psi_{A2}$  are formed by 'positive' and 'negative' combinations of  $\psi_{sp_1(A)}$  and  $\psi_{sp_1(B)}$ , and thus  $\psi_{A1}$  will be more stable than  $\psi_{sp_1}$ , whereas  $\psi_{A2}$  will be less stable than  $\psi_{sp_1}$ . Similarly, the wave functions  $\psi_{B1}$  and  $\psi_{B2}$  are formed by 'positive' and 'negative' combinations of  $\psi_{sp_2(A)}$  and  $\psi_{sp_2(B)}$ , and thus  $\psi_{B1}$  will be more stable than  $\psi_{sp_2}$  whereas  $\psi_{B2}$  will be less stable than  $\psi_{sp_2}$ .

(iii) As mentioned earlier, due to the s-p mixing, the function  $\sigma^*2s$  and  $\sigma^*2p$  are more stabilized whereas  $\sigma 2p$  and  $\sigma^*2p$  are less stabilized (or more destabilized). This conclusion can also be verified from the change in the electron density (or the magnitude of the wave function) in the bond region caused by s-p mixing as described in the following:

The function  $\psi_{+1}$  (or  $\psi_{+2}$ ) have more electron density in the bond region as compared to that of its principal constituent  $\sigma 2s$  (or  $\sigma^*2s$ ). Hence  $\psi_{+1}$  and  $\psi_{+2}$  are more stable as compared to  $\sigma 2s$  and  $\sigma^*2s$ , respectively.

The function  $\psi_{-1}$  (or  $\psi_{-2}$ ) have lesser electron density in the bond region as compared to that of its principal constituent  $\sigma 2p$  (or  $\sigma^*2p$ ). Hence  $\psi_{-1}$  and  $\psi_{-2}$  are less stable as compared to  $\sigma 2p$  and  $\sigma^*2p$ , respectively.

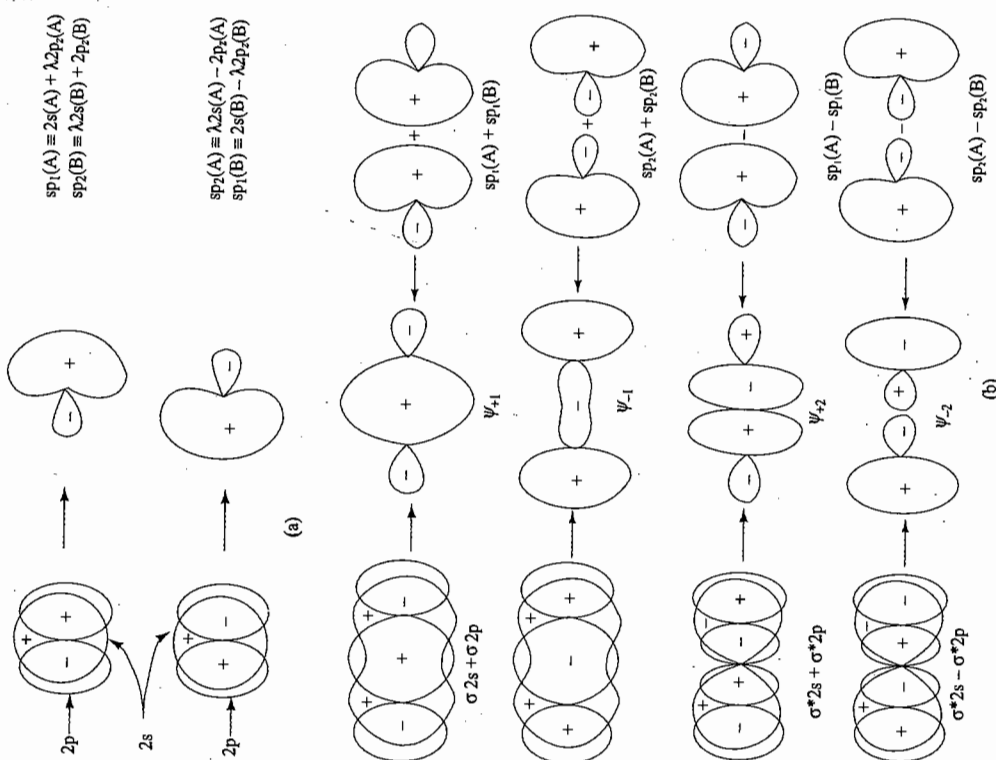


Fig. 2.9.5 Approximate contour diagrams: (a) of hybrid orbitals, (b) of the molecular orbitals obtained via mixing of  $\sigma 2s$  and  $\sigma^*2p$  molecular orbitals and via mixing of sp-hybrid orbitals

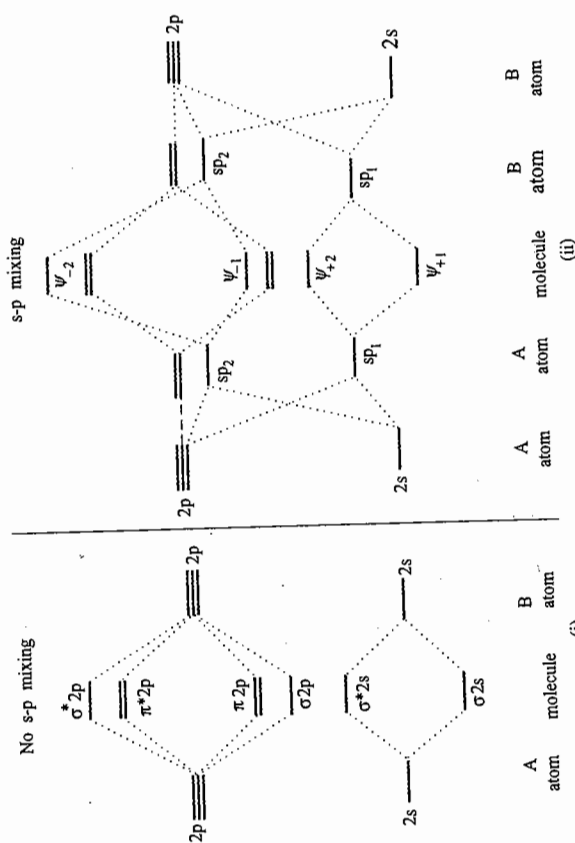


Fig. 2.9.6 Correlation diagrams for homonuclear diatomic molecules exhibiting (i) no s-p mixing, and (ii) s-p mixing viewed from the sp-hybrid orbitals centred on the two atoms

## 2.10 MOLECULAR TERM SYMBOLS

The electronic states of diatomic molecules, like atoms, may be designated by the term symbols. The procedure to determine the term symbol is as follows:

(i) Determine the value of sum of z-component (i.e. along internuclear distance) of orbital angular momentum quantum number.

The expression to be used is

$$M_L = m_{l_1} + m_{l_2} + \dots \quad (2.10.1)$$

(ii) Determine the symbol corresponding to the value of  $|M_L|$ . The symbol corresponding to the magnitude of  $|M_L|$ , which is represented as  $\Lambda$ , is the capital Greek letter as shown in the following:

$ M_L $	0	1	2	3	4
Symbol	$\Sigma$	$\Pi$	$\Delta$	$\Phi$	T

For each nonzero  $\Lambda$  value, there are two  $M_L$  values;  $+\Lambda$  and  $-\Lambda$ ; it is found that the electronic energy depends on  $M_L^2$ , and there is a twofold degeneracy associated with  $\Pi$ ,  $\Delta$ ,  $\Phi$ , ... levels.

(iii) Determine the value of sum of z-component of spin angular momentum quantum numbers.

The expression to be used is

$$M_S = m_{s_1} + m_{s_2} + \dots \quad (2.10.2)$$

- (iv) Ascertain the value of total spin quantum number. From the values of  $M_S$ , the value of  $S$ , which is equal to the maximum value of  $M_S$ , is ascertained.

- (v) Designate the term symbol.

The term symbol is represented as

$$^{2S+1} \left( \begin{array}{c} \text{symbol of} \\ |M_L| \end{array} \right)$$

A few examples are  $^1\Sigma$ ,  $^3\Sigma$  and  $^2\Pi$ .

### A FEW WORKED OUT EXAMPLES

#### $H_2$ molecule

The molecular electronic configuration of  $H_2$  is  $(\sigma_g 1s)^2$ . Thus, we have

$$M_L = m_{l_1} + m_{l_2} = 0 + 0 = 0$$

$$M_S = m_{s_1} + m_{s_2} = (+1/2) + (-1/2) = 0$$

Symbol of  $M_L$  equal to zero is  $\Sigma$ .

Value of  $S$  is 0 ( $= 1/2 - 1/2$ )

Multiplicity of spin,  $2S + 1 = 2 \times 0 + 1 = 1$

Hence, the term symbol is  $^1\Sigma$ .

#### $He_2^+$ species

The molecular electronic configuration of  $He_2^+$  is  $(\sigma_g 1s)^2(\sigma_u 1s)^1$ . Thus, we have

$$M_L = m_{l_1} + m_{l_2} + m_{l_3} = 0 + 0 + 0 = 0$$

$$M_S = m_{s_1} + m_{s_2} + m_{s_3} = (+1/2) + (-1/2) + (\pm 1/2) = \pm 1/2$$

Symbol of  $M_L$  equal to zero is  $\Sigma$ .

Value of  $S$  corresponding to  $M_S = \pm 1/2$  is  $1/2$ .

Multiplicity of spin,  $2S + 1 = 2(1/2) + 1 = 2$

Hence, the term symbol is  $^2\Sigma$ .

#### $B_2$ Molecule

The molecular electronic configuration of  $B_2$  is

$$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^2$$

The first four molecular orbitals need not be considered as their values of  $M_L$  and  $M_S$  are separately equal to zero. For distributing two electrons amongst four spin molecular orbitals of  $\pi$ -type, we proceed as follows:

(i)	$\uparrow$	$\downarrow$	$\square$	$\square$	$m_{l_1} = +1$	$m_{l_2} = +1$	$m_{l_3} = -1/2$	$m_{l_4} = -1/2$	Values of	
					$m_{s_1} = +1$	$m_{s_2} = +1$	$m_{s_3} = -1/2$	$m_{s_4} = -1/2$	$M_L$	$M_S$
(ii)	$\uparrow$	$\square$	$\square$	$\square$					+2	0
(iii)	$\uparrow$	$\square$	$\square$	$\square$					0	+1
(iv)	$\square$	$\downarrow$	$\square$	$\square$					0	0
(v)	$\square$	$\downarrow$	$\square$	$\square$					0	0
(vi)	$\square$	$\square$	$\uparrow$	$\uparrow$					0	-1
									-2	0

### 2.11 HETERONUCLEAR DIATOMIC MOLECULES

- The symbol corresponding to  $|M_L| = 2$  is  $\Delta$ . The associated value of  $M_S$  ( $= 0$ ) indicates that the value of  $S = 0$ . Thus, the value of  $2S + 1 = 1$ . Hence, the term symbol for the entries (i) and (vi) are  $^1\Delta$ .
  - The symbol corresponding to  $M_L$  equal to 0 is  $\Sigma$ . The associated value of  $M_S$  ( $= 1$ ) indicates that the value of  $S = 1$ . Thus, the value of  $2S + 1 = 3$ . The three spin projections associated with this are  $M_S = +1$ ,  $M_S = 0$  and  $M_S = -1$ . Hence, the entries (ii), (iii) and (v) belong to the term symbol  $^3\Sigma$ .
  - The only left out entry is (iv) for which  $M_L = 0$  and  $M_S = 0$ . Hence, its term symbol is  $^1\Sigma$ .
- Thus, for  $B_2$ , there are three possible molecular states. These are  $^1\Sigma$ ,  $^3\Sigma$  and  $^1\Delta$ . Hund's rule is also applicable to molecular states. The ground state of  $B_2$  will be  $^3\Sigma$  as it has the largest spin multiplicity.

The LCAO-MO treatment of homonuclear diatomic molecules can be extended to the heteronuclear diatomic molecules. For example, the molecular orbital of the lowest energy may be constructed by the linear combination of 1s orbitals centred on atoms A and B, respectively.

$$\psi_{MO} = C_1 \psi_{1s(A)} + C_2 \psi_{1s(B)}$$

The energy of the orbital as usual can be determined by applying the variation method to the expression:

$$E = \frac{\langle \psi_{MO} | H_{op} | \psi_{MO} \rangle}{\langle \psi_{MO} | \psi_{MO} \rangle}$$

This will produce two secular equations:

$$C_1 (\alpha_A - E) + C_2 (\beta_{AB} - E \beta_{AB}) = 0$$

$$C_1 (\beta_{AB} - E \beta_{AB}) + C_2 (\alpha_B - E) = 0$$

In order to have nontrivial values of coefficients, we set secular determinant equal to zero, which on expanding will produce a quadratic expression in  $E$ . On solving the latter, we get two roots of energy. These, in turn, can be substituted in the above secular equations to get the coefficients of the two molecular orbitals. In general, the energy of one of the orbitals will be lesser than the smaller of the two energies of atomic orbitals and the other will have larger value than the larger of the two energies of atomic orbitals.

In general, the coefficients  $C_1$  and  $C_2$  are different and depend on the difference in energies  $\alpha_A$  and  $\alpha_B$  (or difference of electronegativity of the two atoms). For the bonding orbital, the coefficient of the larger electronegative atom has a larger value and that for the antibonding orbital, the coefficient is larger for the lesser electronegative atom.

In most cases, the difference of energies of 2s and 2p orbitals is not very large and hence the mixing of 2s and 2p<sub>z</sub> orbitals can also occur. This mixing will lower the energies of  $\sigma$  2s and  $\sigma^*$  2s orbitals whereas those of  $\sigma$  2p and  $\sigma^*$  2p are raised. The heteronuclear diatomic molecules may be classified into two categories. These are:

- One of the atoms is hydrogen and the other contains both s and p valence orbitals. Examples include LiH, HCl, etc.
- Both the atoms contain s and p valence orbitals. Examples include BN, BO, CN, NO, etc.

The relative order of energies of various molecular orbitals for the above two categories along with the electronic configurations of a few molecules is described in the following.

### ONE OF THE ATOMS IS HYDROGEN

In this category, we can have a molecule where H is more electronegative than the other atom (example LiH) or vice versa (example HF). The hydrogen atom contains only one valence orbital which can mix with 2s and 2p<sub>z</sub> orbitals of the other atom. We discuss below the electronic configurations of the molecules LiH and HF.

In LiH, 1s orbital of hydrogen mixes with both 2s and 2p<sub>z</sub> orbitals of Li, and thus produces three molecular orbitals,  $\sigma$ ,  $\sigma^*$  and  $\sigma_z^*$ . The 2p<sub>x</sub> and 2p<sub>y</sub> orbitals do not enter into any combination and thus their energies remain unaffected. Such orbitals are known as nonbonding orbitals. The relative order of energies of various orbitals is shown in Fig. 2.11.1. The lowest orbital  $\sigma$ , which is more stable than 1s orbital of hydrogen, is mainly composed of hydrogen 1s orbital with smaller fractions of lithium 2s and 2p<sub>z</sub> orbitals.

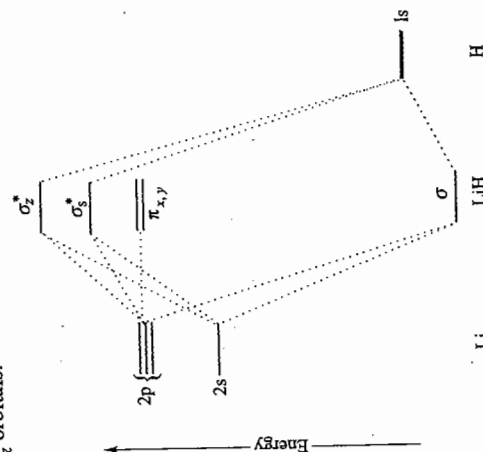
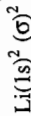


Fig. 2.11.1 Correlation diagram of LiH

The  $\sigma_z^*$  orbital has energy greater than  $\pi_x$  and  $\pi_y$  orbitals with much greater weightage of lithium 2s orbital. The  $\sigma_z^*$  orbital is less stable than that of 2p<sub>z</sub> orbital of lithium and has considerable p<sub>z</sub> character. The electronic configuration of LiH is



Determine the partial ionic character of LiH by evaluating the Mullikan gross atomic population numbers. Given:

- The lowest bonding molecular orbital

$$\sigma = 0.700 \psi_{1s(H)} + 0.328 \psi_{2s(Li)} + 0.204 \psi_{2p_z(Li)}$$

- Overlap integrals:  $S(1s(H); 2s(Li)) = 0.469$  and  $S(1s(H); 2p_z(Li)) = 0.506$

The electron density in LiH is obtained by squaring the molecular orbital  $\sigma$  and then multiplying it by its occupancy number (i.e. 2). Thus we have

$$\begin{aligned} \rho &= 2 (0.700 \psi_{1s(H)} + 0.328 \psi_{2s(Li)} + 0.204 \psi_{2p_z(Li)})^2 \\ &= 0.98 \psi_{1s(H)}^2 + 0.215 \psi_{2s(Li)}^2 + 0.083 \psi_{2p_z(Li)}^2 \\ &\quad + 0.918 \psi_{1s(H)} \psi_{2s(Li)} + 0.571 \psi_{1s(H)} \psi_{2p_z(Li)} + 0.268 \psi_{2s(Li)} \psi_{2p_z(Li)} \end{aligned}$$

The above density consists of atomic-orbital densities like  $\psi_{1s(H)}^2$ ,  $\psi_{2s(Li)}^2$  and  $\psi_{2p_z(Li)}^2$  and overlap densities like  $\psi_{1s(H)} \psi_{2s(Li)}$ ,  $\psi_{1s(H)} \psi_{2p_z(Li)}$  and  $\psi_{2s(Li)} \psi_{2p_z(Li)}$ . To get the relative Mullikan gross atomic population numbers, the coefficient of overlap density is multiplied by the overlap integral involving the two orbitals and then it is divided by 2. The resultant number is assigned as the coefficient of atomic-orbital densities involving the two atomic orbitals, i.e.

$$C \psi_A \psi_B = \frac{C}{2} S_{AB} (\psi_A^2 + \psi_B^2)$$

$$\begin{aligned} \text{Hence, } 0.918 \psi_{1s(H)} \psi_{2s(Li)} &= \frac{0.918}{2} S(1s(H); 2s(Li)) (\psi_{1s(H)}^2 + \psi_{2s(Li)}^2) \\ &= \frac{0.918 \times 0.469}{2} (\psi_{1s(H)}^2 + \psi_{2s(Li)}^2) \\ &= 0.215 \psi_{1s(H)}^2 + 0.215 \psi_{2s(Li)}^2 \end{aligned}$$

$$\begin{aligned} 0.571 \psi_{1s(H)} \psi_{2p_z(Li)} &= \frac{0.571}{2} S(1s(H); 2p_z(Li)) (\psi_{1s(H)}^2 + \psi_{2p_z(Li)}^2) \\ &= \frac{0.571 \times 0.506}{2} (\psi_{1s(H)}^2 + \psi_{2p_z(Li)}^2) \\ &= 0.145 \psi_{1s(H)}^2 + 0.145 \psi_{2p_z(Li)}^2 \end{aligned}$$

$$\begin{aligned} 0.268 \psi_{2s(Li)} \psi_{2p_z(Li)} &= \frac{0.268}{2} S(2s(Li); 2p_z(Li)) (\psi_{2s(Li)}^2 + \psi_{2p_z(Li)}^2) \\ &= (\text{zero}) \psi_{2s(Li)}^2 + (\text{zero}) \psi_{2p_z(Li)}^2 \end{aligned}$$

Thus, the gross-atomic population numbers are

$$n_{1s(H)} = 0.98 + 0.215 + 0.145 = 1.340$$

$$n_{2s(Li)} = 0.215 + 0.215 = 0.430$$

$$n_{2p_z(Li)} = 0.083 + 0.145 = 0.228$$

$$\text{Total charge on Li atom} = 0.430 + 0.228 \approx 0.66$$

Hence Li carries  $1 - 0.66 = 0.34$  positive charge

whereas H carries  $1.34 - 1 = 0.34$  negative charge

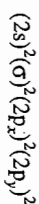
Thus, LiH may be written as  $\text{Li}^{+0.34} \text{H}^{-0.34}$



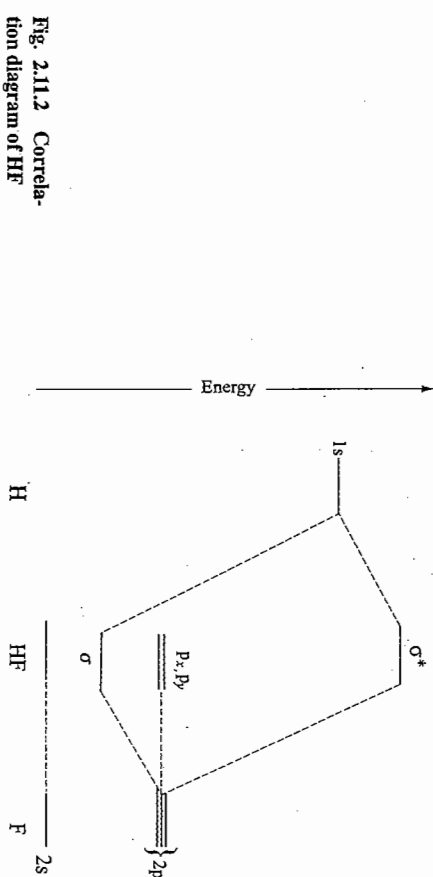
**Hydrogen Fluoride**

The energies of  $1s(\text{H})$ ,  $2s(\text{F})$  and  $2p_z(\text{F})$  correspond to  $-110 \times 10^3 \text{ cm}^{-1}$ ,  $-374 \times 10^3 \text{ cm}^{-1}$  and  $-151 \times 10^3 \text{ cm}^{-1}$ , respectively. The  $2s(\text{F})$  orbital energy is much lower than that of  $1s(\text{H})$  and that of  $2p_z(\text{F})$  is closer to that of  $1s(\text{H})$ . It may be assumed that an effective combination takes place only between  $1s(\text{H})$  and  $2p_z(\text{F})$  orbitals. The orbitals  $2s(\text{F})$ ,  $2p_x(\text{F})$  and  $2p_y(\text{F})$  remain unaffected in the bonding formation and thus are nonbonding orbitals. Since electrons are pulled toward the atom that has the larger electronegativity, it is expected that in the bonding orbital  $\sigma$ , the coefficient of  $\psi_{2p_z(\text{F})}$  will be much larger than that of  $\psi_{1s(\text{H})}$ . In the antibonding orbital, the reverse will be true, i.e. the coefficient of  $\psi_{1s(\text{H})}$  will be larger than that  $\psi_{2p_z(\text{F})}$ .

The relative order of energies of molecular orbitals in HF is shown in Fig. 2.11.2. There are ten electrons in HF molecule, two of which are occupied by  $1s(\text{F})$  orbital. The remaining eight valence electrons can be placed as follows:



There will be one sigma bond and three lone pairs in the three nonbonding orbitals. This arrangement corresponds to the Lewis structure  $(\text{H} \rightarrow \ddot{\text{F}}:)$ .

**Correlation Diagram for AB Molecule****BOTH ATOMS CONTAIN s AND p VALENCE ORBITALS**

Let the atom B in the molecule AB be more electronegative than A. The energy of an atomic orbital of atom B will have a smaller value than that of the corresponding orbital of atom A. The formation of  $\sigma$  and  $\pi$  bonding and antibonding molecular orbitals in AB molecule is similar to those of homonuclear diatomic molecule. The shape of molecular orbitals is not symmetrical. This is due to the fact that the coefficient of orbital belonging to the more electronegative atom has a larger value in the bonding orbital and lesser value in the antibonding orbital.

Fig. 2.11.3 Relative order of energies in an AB molecule; atom B is more electronegative than A

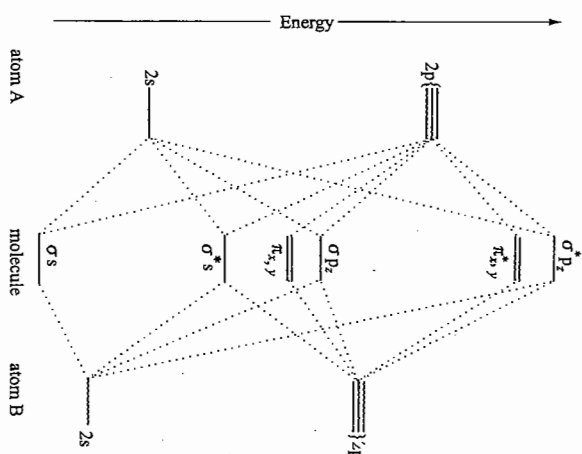


Figure 2.11.3 displays the relative orbital energies in AB molecule. Figure 2.11.4 displays the boundary surfaces of some of the molecular orbitals of an AB molecule.

Table 2.11.1 records the electronic configurations of a few diatomic molecules.

Table 2.11.1 The Lowest Electronic Configurations of a Few Heteronuclear Diatomic Molecules

Number of valence electrons	Molecule	Electronic configuration	Dissociation energy kJ mol <sup>-1</sup>	Bond order	Bond length pm
8	BN	$(\sigma s)^2(\sigma^* s)^2(\pi_x)^3(\sigma p_z)$	384.9	2	128
9	BO		774.0	2.5	120
	CN	$(\sigma s)^2(\sigma^* s)^2(\pi_x)^4(\sigma p_z)$	786.6		117
	CO <sup>+</sup>				111.5
10	CO	$(\sigma s)^2(\sigma^* 2s)^2(\pi_x)^4(\sigma p_z)^2$	1070.3	3	112.8
	NO <sup>+</sup>				106.2
	CN <sup>-</sup>				114
11	NO	$(\sigma s)^2(\sigma^* s)^2(\pi_x)^4(\sigma p_z)^2(\pi_x^*)^1$	667.8	2.5	115



have been derived following the LCAO scheme. There is another approach, known as united-atom concept, which enables us to find the shapes and energies of various molecular orbitals of a diatomic molecule. In this method, an united atom, formed as a result of coalescence of two nuclei, is considered. Then the two nuclei are imagined to be gradually separated. As the separation is increased from zero to infinite distance, the united atom will pass over to the diatomic molecule and then finally to the separated atoms. During this process, it is expected that the atomic orbitals of the united atom will gradually change to the appropriate molecular orbitals of the molecule and finally to the appropriate atomic orbitals of the separated atoms. Consequently, it is expected that the energies of the united atomic orbitals will change smoothly (not necessarily linear) to the energies of appropriate molecular orbitals and finally to the energies of appropriate atomic orbitals of the separated atoms. The above relationship between the orbitals of the three different systems, viz., united atom, molecule and separated atoms, is exhibited by the *correlation diagram*. In this, the energies of various united atomic orbitals are displayed at one extreme and those of separated atoms at the other extreme and then these energies are connected to exhibit the appropriate transformations.

Before we draw such diagrams, it is worth considering the example of  $H_2$  molecule. In the united atom concept, we consider He atom and then separate the two protons along some axis, say, the z-axis. The behaviour of the orbitals of the first three principal energy levels of the united atom as this separation is slowly increased is shown in Fig. 2.12.1.

### Classification of Orbitals

An examination of the orbitals in Fig. 2.12.1 reveals that the various orbitals may be classified into two categories as follows.

1. United-atomic orbitals which on separation produce atomic orbitals of the same principal quantum number. These are:  $1s$ ,  $2s$ ,  $2p_x$ ,  $2p_y$ ,  $2p_z$ ,  $3d_{z^2}$ ,  $3d_{xy}$  and  $3d_{x^2-y^2}$ . The energy of this category of orbitals increases rapidly as the nuclei are separated because the nuclear charge is halved in the separated atoms, and we are dealing with the same principal quantum number. Conversely, we may state that the energy of an orbital in this category decreases (not necessarily linearly) as the nuclear separation decreases. Thus, these orbitals constitute the bonding orbitals.
2. United-atomic orbitals which on separation produce atomic orbitals of the next inner principal quantum number. These are:  $2p_z$ ,  $3s$ ,  $3p_x$ ,  $3d_{z^2}$  and  $3d_{xy}$  orbitals. The energy of this category of orbitals decreases as the nuclei are separated, owing to the change in the principal quantum number. If the energy of an orbital increases as the nuclear separation is decreased, then it behaves as an antibonding orbital.

Since the energy difference between the united-atom orbitals of this category and the separated atomic orbitals is relatively small, the prediction of the energy of the orbitals at intermediate distances is not so simple. In fact, the energy of a given orbital may exhibit a maximum or a minimum. For example, the energy level of  $3s$  united-atomic orbital exhibits a minimum at a normal bond distance (not shown in Fig. 2.12.2). This minimum lies below the  $2p$  orbital of separated atom and hence behaves as the bonding orbital.

Figure 2.12.2 displays the correlation diagram for molecular orbitals in homonuclear diatomic molecules. This diagram incorporates the variation in energies

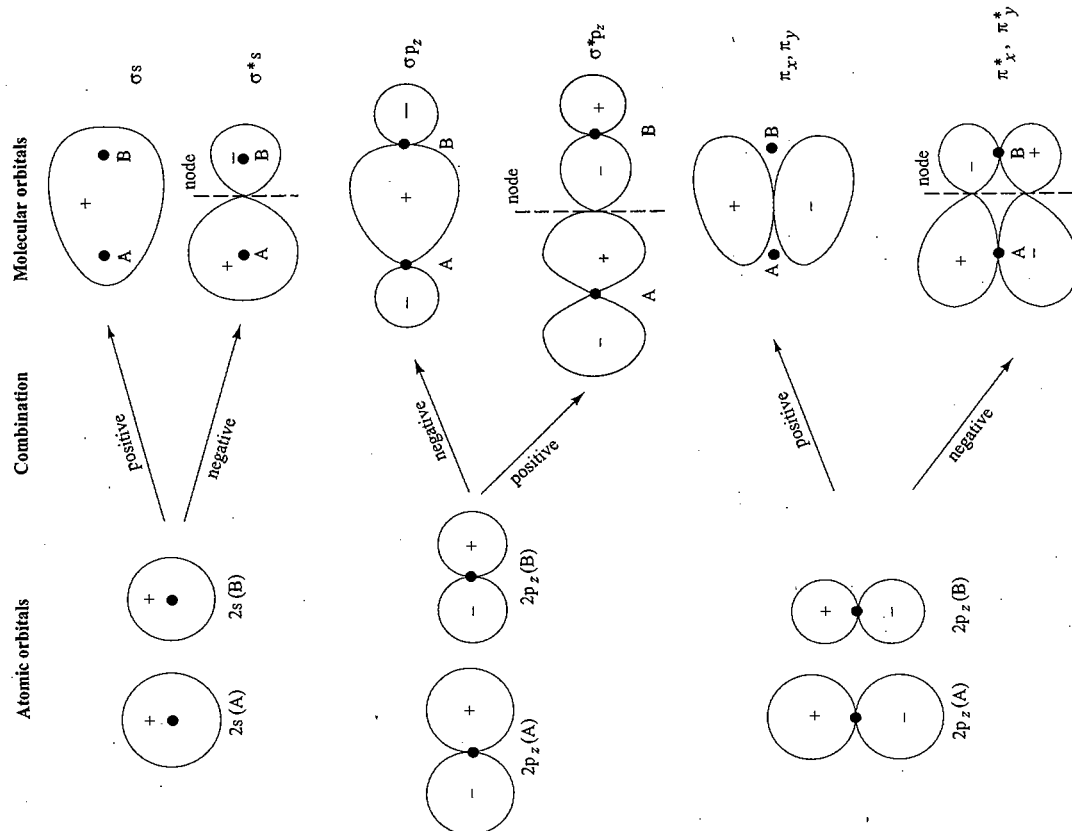


Fig. 2.11.4 Shapes of the molecular orbitals of an AB molecule; atom B is more electronegative than A. The approximate representation involving only angular functions for 2p orbitals is used

### 2.12 UNITED-ATOM CONCEPT AND THE CORRELATION DIAGRAMS

#### Description of the Concept

So far, we have considered the formation of a diatomic molecule from the viewpoint of bringing two atoms close together from a large distance to the internuclear distance of the molecule. The shapes and energies of various molecular orbitals

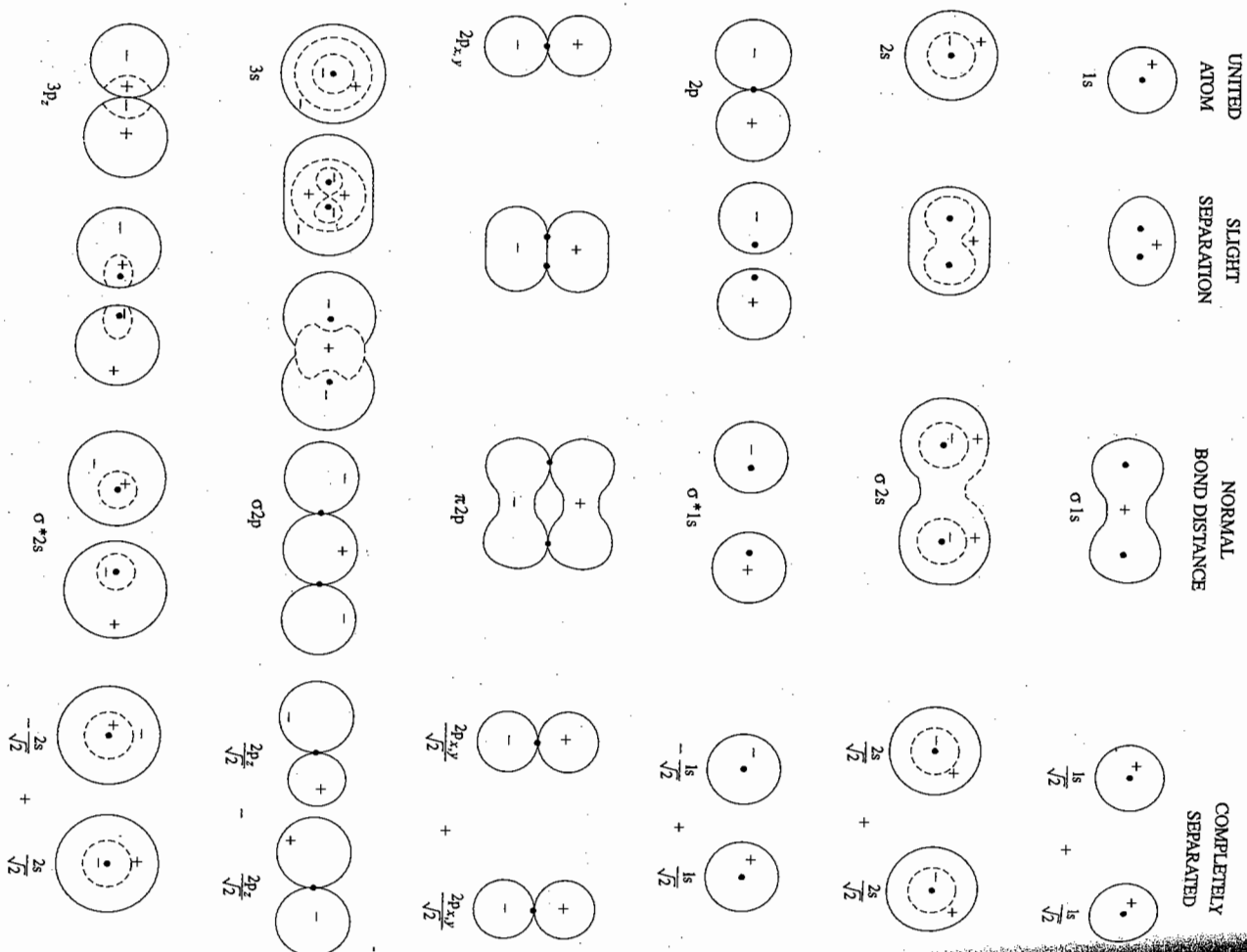
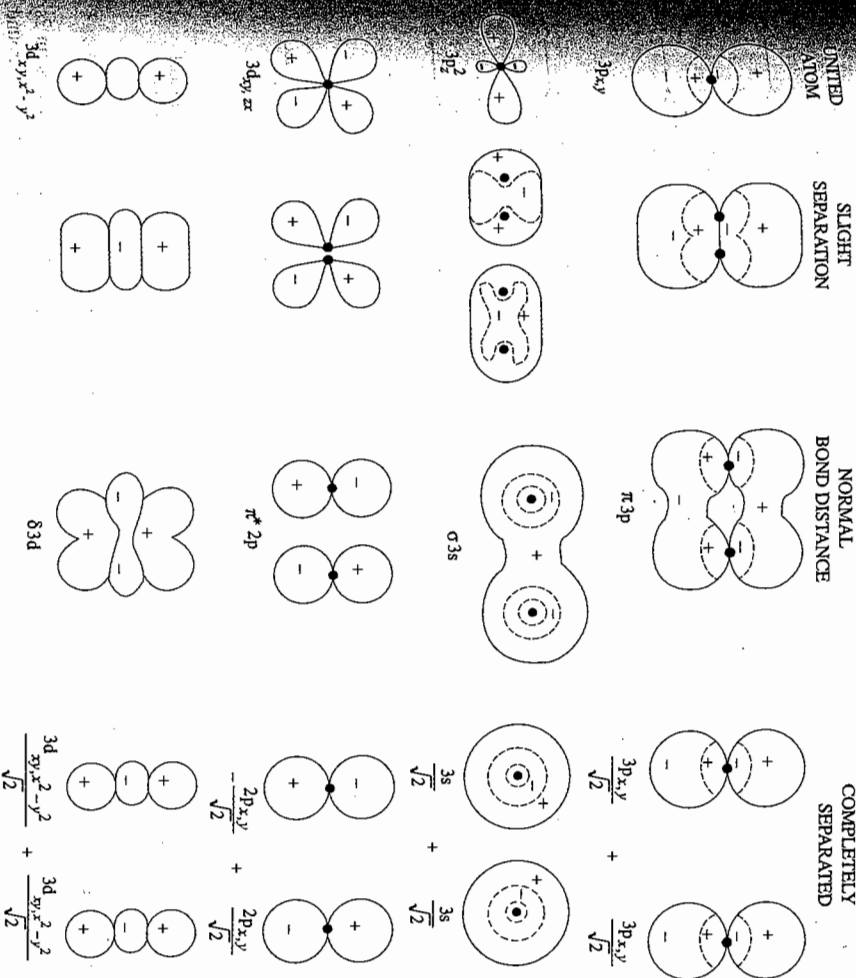


Fig. 2.12.1 (continued)

Fig. 2.12.1 The change in the shapes of He<sup>+</sup> orbitals with the separation of two nuclei

of the two types of orbitals discussed above. Consulting this diagram, we can write down the relative order of energies of molecular orbitals at the given internuclear distance. For example, at the two distances shown in Fig. 2.12.2, the relative orders are:

$$\begin{aligned} \text{At } r = r_A \quad & \sigma_g 1s < \sigma_u 1s < \sigma_g 2s < \sigma_u 2s < \pi_u 2p < \pi_g 2p < \sigma_u 2p \\ \text{At } r = r_B \quad & \sigma_g 1s < \sigma_u 1s < \sigma_g 2s < \pi_u 2p < \pi_g 2p < \sigma_u 2p \end{aligned}$$

Thus knowing the internuclear distance of a diatomic molecule, we can write down its electronic configuration by consulting the correlation diagram.

There is one universal rule which holds good in the correlation diagram and must be highlighted here. This rule, which is known as the *non-crossing rule*, states that if the potential energy curves for a diatomic molecule are plotted as functions of internuclear distance, then the curves for the two states having the same symmetry cannot cross one another. This rule helps correlating the molecular orbital with the

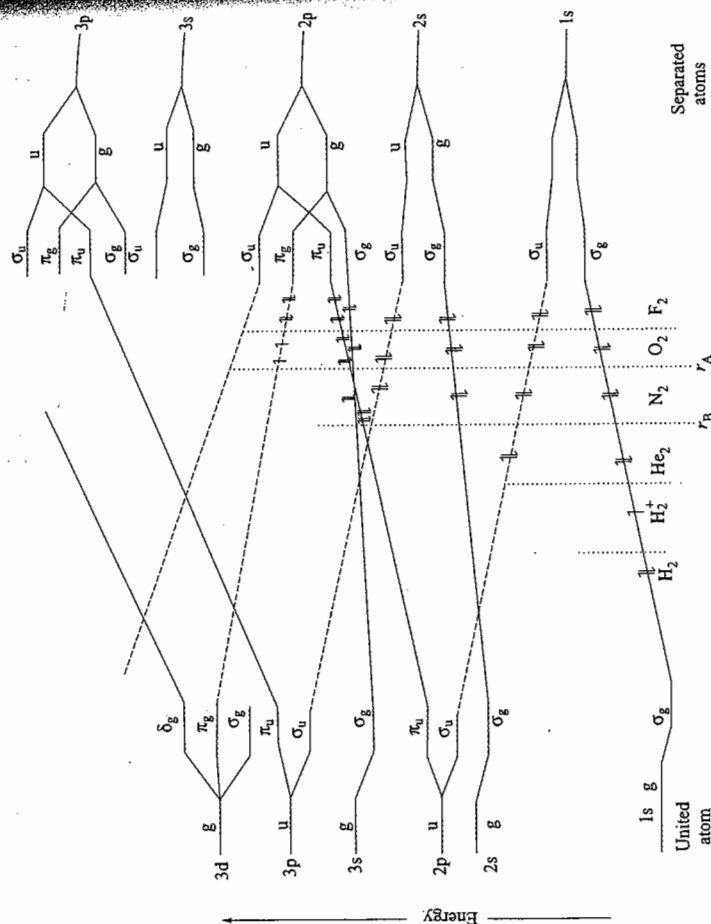


Fig. 2.12.2 Correlation diagram for homonuclear diatomic molecules (schematic)

united-atom orbital. For example,  $\sigma_g 2s$  must correlate with the united atom  $2s$  orbital, and the  $\sigma_g 2p$  with the united atom  $3s$  orbital, and not the other way around as it will violate the non-crossing rule.

**Correlation Diagram** The correlation diagram for the heteronuclear diatomic molecules is shown in Fig. 2.12.3, and it can be used to write down the electronic configurations of diatomic molecules.

## 2.13 HYBRID ORBITALS

### Explanation of Hybrid Orbitals

Though the chemical bonding in a polyatomic molecule can be described under the LCAO-MO framework, yet the very basic concept of chemistry of localized bonds between particular atoms in the molecule is completely lost as the molecular orbitals are delocalized over the entire molecule. However, Lennard-Jones and his coworkers have shown that the delocalized molecular orbitals can be transformed into the localized molecular orbitals (known as *equivalent orbitals*) through mathematical transformations.

Alternatively, the formation of the localized bonds may be explained by the overlapping between the *hybrid orbitals* of the one atom with the atomic orbitals

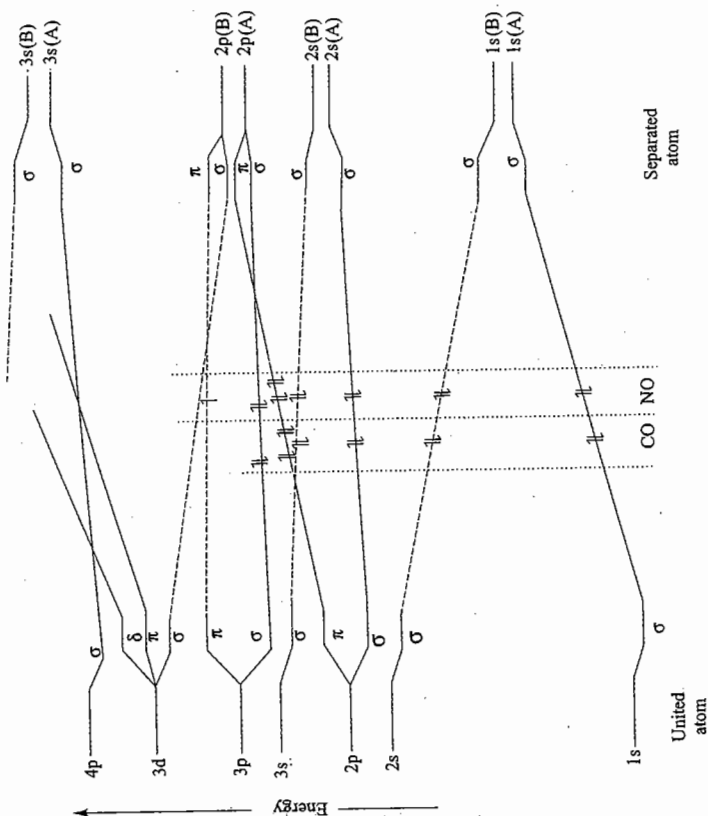


Fig. 2.12.3 Correlation diagram for heteronuclear diatomic molecules (only schematic)

or hybrid orbitals of the other atom (valence bond approach). The hybrid orbitals are formed by the linear combination of atomic orbitals centred on the same atom. Taking the simplest example of Be atom, we find that its electronic configuration is  $(1s)^2(2s)^2$ . Since the Be atom does not contain any unpaired electron, its combining capacity with other atom should be zero. But invariably it is found to be divalent. However, its divalent nature may be explained by promoting one of the 2s-electrons to the 2p orbital. Such a situation may be described by the determinant

$$|(\psi_{2s} \alpha) (\psi_{2p_z} \alpha)| \quad (2.13.1)$$

For the configuration given by Eq. (2.13.1), we may expect the formation of two different types of bonds as the 2s orbital is nondirectional and 2p orbital has directional characteristics. But in reality the two bonds formed are completely identical in nature, and are oriented at an angle of  $180^\circ$  with each other.

It can be shown that the wave function as given by the determinant of Eq. (2.13.1) remains unchanged when each column in the latter is replaced by the following linear combinations of 2s and 2p orbitals:

$$\psi_1 = \frac{1}{\sqrt{2}} (\psi_{2s} + \psi_{2p_z}) \quad (2.13.2)$$

$$\psi_2 = \frac{1}{\sqrt{2}} (\psi_{2s} - \psi_{2p_z}) \quad (2.13.3)$$

The functions  $\psi_1$  and  $\psi_2$  describe the hybrid orbitals of Be atom. (Note that  $2s$  and  $2p_z$  orbitals in Eqs (2.13.2) and (2.13.3) belong to the same atom.) The orbitals  $\psi_1$  and  $\psi_2$  are completely identical in size, shape, energy and directional characteristics.

In general, the number of hybrid orbitals formed is equal to the number of atomic orbitals that are being combined to form hybrid orbitals. Thus, by mixing one  $2s$  and two  $2p$  orbitals, we get three equivalent  $sp^2$  hybrid atomic orbitals and mixing of one  $2s$  and three  $2p$  atomic orbitals produces four equivalent  $sp^3$  hybrid atomic orbitals.

In general, hybrid orbitals from  $s$  and  $p$  orbitals have two lobes, one of which is highly enhanced and the other one is highly shortened. As a consequence, a better overlapping between the hybrid orbital and the orbital of other atom is produced. The orbital of the other atom may be simply an atomic orbital or a hybrid atomic orbital. Thus, a hybrid orbital can form a better bond as compared to that formed from the atomic orbital.

The wave functions of  $sp$ ,  $sp^2$  and  $sp^3$  hybrid orbitals can be derived by following the guidelines given below.

- The charge density of  $s$  orbital will be equally distributed amongst the possible hybrid orbitals. If there are  $n$  hybrid orbitals, then square of the coefficient of  $s$  orbitals in all the  $n$  hybrid orbitals will have the same value of  $1/n^2$ .

- The atomic wave functions constitute the orthonormal set, such that

$$\int \psi_i \psi_j d\tau = 1 \quad (2.13.4)$$

$$\int \psi_i \psi_j d\tau = 0 \quad (2.13.5)$$

- The formed hybrid orbitals also constitute orthonormal set, i.e. for them also the above expressions are applicable.

- For  $sp^2$  hybridization, we may assume that the first hybrid orbital to be derived has its maximum on  $x$ -axis. Thus, this orbital will not include any contribution from  $p_y$  or  $p_z$  orbital.

- For  $sp^3$  hybridization, we may assume that the second orbital lies in a plane, say, on  $xz$ -plane. Thus, this orbital will not include any contribution from  $p_y$  orbital.

Following the guidelines given above, we now derive the wave functions and their characteristics for  $sp$ ,  $sp^2$  and  $sp^3$  hybrid orbitals.

### sp HYBRID ORBITALS

#### Wave Functions of sp Hybrid Orbitals

For the two hybrid orbitals, we may write

$$\psi_1 = a_1 \psi_s + b_1 \psi_p$$

$$\psi_2 = a_2 \psi_s + b_2 \psi_p$$

- (i) Since the charge density of  $s$  orbital is equally divided between the two hybrid orbitals, we may write

$$a_1^2 = a_2^2 = \frac{1}{2} \quad \text{i.e.} \quad a_1 = a_2 = \frac{1}{\sqrt{2}}$$

- (ii) Since  $\psi_1$  is normalized, we may write

$$\int \psi_1^2 d\tau = a_1^2 \int \psi_s^2 d\tau + b_1^2 \int \psi_p^2 d\tau + 2a_1 b_1 \int \psi_s \psi_p d\tau = 1$$

Since atomic orbitals are orthogonal, we may write the above expression as

$$a_1^2 + b_1^2 = 1$$

Now since  $a_1^2 = 1/2$ , we get

$$b_1 = \frac{1}{\sqrt{2}}$$

- (iii) Since  $\psi_1$  and  $\psi_2$  are orthogonal, we may write

$$a_1 a_2 + b_1 b_2 = 0$$

Substituting the values of  $a_1$ ,  $a_2$  and  $b_1$ , we get

$$\left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right) + \left(\frac{1}{\sqrt{2}}\right)b_2 = 0$$

$$\text{or} \quad b_2 = -\frac{1}{\sqrt{2}}$$

Hence, the two functions are

$$\psi_1 = \frac{1}{\sqrt{2}} (\psi_s + \psi_p) \quad (2.13.6)$$

$$\psi_2 = \frac{1}{\sqrt{2}} (\psi_s - \psi_p) \quad (2.13.7)$$

To derive angle and general shape of hybrid orbitals, we take the radius of spherical contour surface, representing the magnitude of the  $s$ -orbital, to be equal to 1. Relative to this unit, the magnitudes of the  $p$  orbitals, which vary due to the angular dependence, are

$$p_z = \sqrt{3} \cos \theta \quad (2.13.8)$$

$$p_x = \sqrt{3} \sin \theta \cos \phi \quad (2.13.9)$$

$$p_y = \sqrt{3} \sin \theta \sin \phi \quad (2.13.10)$$

where  $\theta$  is the angle of a vector with  $z$ -axis and  $\phi$  is the angle of the projection of the vector on  $xy$ -plane with the  $x$ -axis.

Utilizing the above relations, Eqs (2.13.6) and (2.13.7) may be written as

$$\psi_1 = \frac{1}{\sqrt{2}} (1 + \sqrt{3} \cos \theta) \quad (2.13.11)$$

$$\psi_2 = \frac{1}{\sqrt{2}} (1 - \sqrt{3} \cos \theta) \quad (2.13.12)$$

### Shapes of the Two Orbitals

Since the above functions do not contain any  $\varphi$ , it is obvious that both the functions lie on  $z$ -axis and hence the angle between them must be  $180^\circ$ .

The function  $\psi_1$  will have its maximum when  $\theta = 0$ . This maximum relative to  $s$  orbital has a value of  $1 + \sqrt{3}$  (= 2.732). The corresponding value for  $p_z$  orbital is  $\sqrt{3}$  (= 1.732).

Thus, it is obvious that the  $sp$  hybrid orbital will be better than  $p_z$  orbital as far as overlapping with the orbital of another atom is concerned, resulting in a better bond.

The functions  $\psi_1$  and  $\psi_2$  when plotted against different values of  $\theta$  give the shapes as shown in Fig. 2.13.1.

Examples forming  $sp$  orbitals include Be and C (acetylene).

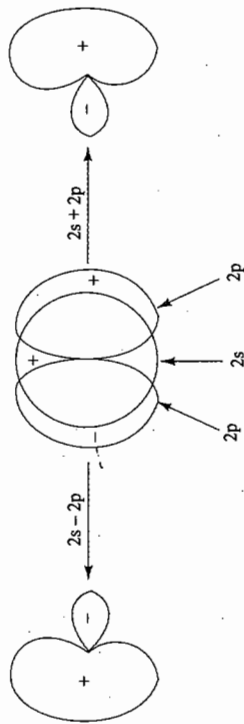


Fig. 2.13.1 Schematic representation of  $sp$  hybridization

### $sp^2$ HYBRID ORBITALS

For the three hybrid orbitals, we may write

$$\psi_1 = a_1 \psi_s + b_1 \psi_{p_x} + c_1 \psi_{p_y}$$

$$\psi_2 = a_2 \psi_s + b_2 \psi_{p_x} + c_2 \psi_{p_y}$$

$$\psi_3 = a_3 \psi_s + b_3 \psi_{p_x} + c_3 \psi_{p_y}$$

(i) Since the charge density of  $s$  orbital is equally divided among the three hybrid orbitals, we get

$$a_1^2 = a_2^2 = a_3^2 = \frac{1}{3} \quad \text{i.e.} \quad a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}$$

(ii) If we assume  $\psi_1$  to point towards  $x$ -axis, then the contribution of  $p_y$  orbital in this will be zero, i.e.

$$c_1 = 0$$

(iii) Normalization condition of  $\psi_1$  gives

$$a_1^2 + b_1^2 = 1$$

Since  $a_1 = 1/\sqrt{3}$ , we get

$$b_1 = \sqrt{\frac{2}{3}}$$

(iv) Orthogonal conditions of  $\psi_1$  and  $\psi_2$ , and  $\psi_1$  and  $\psi_3$  give

$$a_1 a_2 + b_1 b_2 = 0$$

$$a_1 a_3 + b_1 b_3 = 0$$

$$\text{Hence } b_2 = -\frac{a_1 a_2}{b_1} = -\frac{1/3}{\sqrt{2/3}} = -\frac{1}{\sqrt{6}}$$

$$b_3 = -\frac{a_1 a_3}{b_1} = -\frac{1/3}{\sqrt{2/3}} = -\frac{1}{\sqrt{6}}$$

(v) Normalization condition of  $\psi_2$  gives  $a_2^2 + b_2^2 + c_2^2 = 1$

$$\text{Hence } c_2^2 = 1 - (a_2^2 + b_2^2) = 1 - \left(\frac{1}{3} + \frac{1}{6}\right) = \frac{1}{2} \quad \text{or } c_2 = \frac{1}{\sqrt{2}}$$

(vi) Normalization condition of  $\psi_3$  gives

$$a_3^2 + b_3^2 + c_3^2 = 1$$

$$c_3^2 = 1 - (a_3^2 + b_3^2) = 1 - \left(\frac{1}{3} + \frac{1}{6}\right) = \frac{1}{2}$$

$$c_3 = -\frac{1}{\sqrt{2}}$$

(For  $\psi_2$  and  $\psi_3$  to be different, we take the minus root of  $c_3$ .)

Hence three functions are

$$\psi_1 = \frac{1}{\sqrt{3}} \psi_s + \sqrt{\frac{2}{3}} \psi_{p_x} \quad (2.13.13)$$

$$\psi_2 = \frac{1}{\sqrt{3}} \psi_s - \frac{1}{\sqrt{6}} \psi_{p_x} + \frac{1}{\sqrt{2}} \psi_{p_y} \quad (2.13.14)$$

$$\psi_3 = \frac{1}{\sqrt{3}} \psi_s - \frac{1}{\sqrt{6}} \psi_{p_x} - \frac{1}{\sqrt{2}} \psi_{p_y} \quad (2.13.15)$$

Utilizing the expressions of Eqs (2.13.8) to (2.13.10), we get

$$\psi_1 = \frac{1}{\sqrt{3}} + \sqrt{\frac{2}{3}} \sqrt{3} \sin \theta \cos \varphi$$

$$\psi_2 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{6}} \sqrt{3} \sin \theta \cos \varphi + \frac{1}{\sqrt{2}} \sqrt{3} \sin \theta \sin \varphi$$

$$\psi_3 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{6}} \sqrt{3} \sin \theta \cos \varphi - \frac{1}{\sqrt{2}} \sqrt{3} \sin \theta \sin \varphi$$

Since the  $p_z$  orbital does not appear in Eqs (2.13.13) to (2.13.15), we may conclude that all three orbitals lie in the  $xy$ -plane for which angle  $\theta$  is equal to  $90^\circ$ . Thus, the above relations become

$$\psi_1 = \frac{1}{\sqrt{3}} + \sqrt{2} \cos \varphi \quad (2.13.16)$$

$$\psi_2 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}} \cos \varphi + \sqrt{\frac{3}{2}} \sin \varphi \quad (2.13.17)$$

$$\psi_3 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{2}} \cos \phi - \sqrt{\frac{3}{2}} \sin \phi \quad (2.13.18)$$

Let  $\psi_1$  have its maximum on x-axis. In order to find the direction of maximum of  $\psi_2$ , we equate  $d\psi_2/d\phi = 0$ . Thus, we have

$$\frac{d\psi_2}{d\phi} = \frac{1}{\sqrt{2}} \sin \phi + \sqrt{\frac{3}{2}} \cos \phi = 0$$

$$\text{or } \tan \phi = -\frac{\sqrt{3}}{\sqrt{2}} \sqrt{2} = -\sqrt{3} = -1.732$$

$$\text{Hence } \phi = 120^\circ$$

Thus, the three hybrid orbitals are inclined at an angle of  $120^\circ$  with each other.

The function  $\psi_1$  will have its maximum, say on x-axis, for which  $\phi = 0$ . This maximum relative to s orbital has a value of  $1 + \sqrt{2} = 2.414$ . In comparison to  $p_x$  orbital ( $\theta = 90^\circ$ ,  $\phi = 0$ , maximum = 1.732), the  $sp^2$  orbital is better in overlapping with the orbital of another atom. The function  $\psi_1$ ,  $\psi_2$  and  $\psi_3$  when plotted against different values of  $\phi$  give the orbitals (only schematic) as shown in Fig. 2.13.2.

Examples forming  $sp^2$  orbitals include B and C (ethylene).

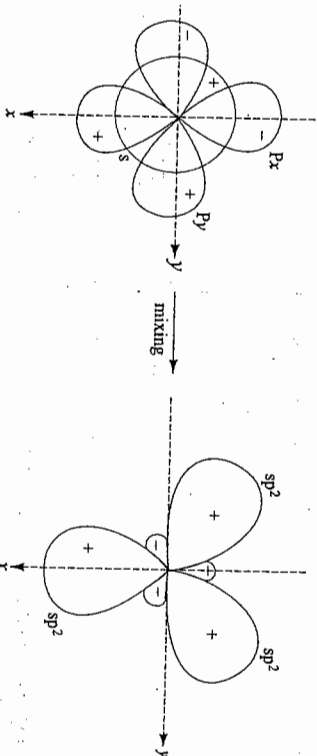


Fig. 2.13.2 Schematic plots of  $sp^2$  hybridization. The correct shape of  $sp^2$  hybrid orbital is shown in Fig. 2.13.4

### Wave Functions of $sp^3$ Hybrid Orbitals

#### $sp^3$ HYBRID ORBITALS

For the four hybrid orbitals, we may write

$$\psi_1 = a_1\psi_s + b_1\psi_{p_x} + c_1\psi_{p_y} + d_1\psi_{p_z}$$

$$\psi_2 = a_2\psi_s + b_2\psi_{p_x} + c_2\psi_{p_y} + d_2\psi_{p_z}$$

$$\psi_3 = a_3\psi_s + b_3\psi_{p_x} + c_3\psi_{p_y} + d_3\psi_{p_z}$$

$$\psi_4 = a_4\psi_s + b_4\psi_{p_x} + c_4\psi_{p_y} + d_4\psi_{p_z}$$

(i) Since the charge density of s orbital is to be distributed equally over all the four orbitals, we write

$$a_1^2 = a_2^2 = a_3^2 = a_4^2 = \frac{1}{4} \quad \text{or} \quad a_1 = a_2 = a_3 = a_4 = \frac{1}{2}$$

(ii) Let us develop  $\psi_1$  on the x-axis. It is obvious that the contribution of  $\psi_{p_y}$  and  $\psi_{p_z}$  in the function  $\psi_1$  will be zero and hence we may write

$$c_1 = 0 \quad \text{and} \quad d_1 = 0$$

(iii) Normalization of  $\psi_1$  gives

$$a_1^2 + b_1^2 = 1 \quad \text{or} \quad b_1^2 = 1 - a_1^2 = 1 - \frac{1}{4} = \frac{3}{4}$$

$$\text{Hence } b_1 = \frac{\sqrt{3}}{2}$$

(iv) Orthogonal conditions of  $\psi_1$  and  $\psi_2$ ,  $\psi_1$  and  $\psi_3$ , and  $\psi_1$  and  $\psi_4$  give

$$a_1a_2 + b_1b_2 = 0$$

$$a_1a_3 + b_1b_3 = 0$$

$$a_1a_4 + b_1b_4 = 0$$

$$\text{Hence } b_2 = b_3 = b_4 = -\frac{a_1a_2}{b_1} = -\frac{1/4}{\sqrt{3}/2} = -\frac{1}{2\sqrt{3}}$$

(v) We assume that  $\psi_2$  lies on xz-plane. Hence the contribution of  $p_y$  in  $\psi_2$  will be zero, i.e.

$$c_2 = 0$$

(vi) Normalization condition of  $\psi_2$  gives

$$a_2^2 + b_2^2 + d_2^2 = 1$$

$$\text{or } d_2^2 = 1 - (a_2^2 + b_2^2) = 1 - \left(\frac{1}{4} + \frac{1}{12}\right) = 1 - \frac{1}{3} = \frac{2}{3}$$

$$d_2 = \sqrt{\frac{2}{3}}$$

(vii) Orthogonal condition of  $\psi_2$  and  $\psi_3$ , and  $\psi_2$  and  $\psi_4$  gives

$$a_2a_3 + b_2b_3 + d_2d_3 = 0$$

$$a_2a_4 + b_2b_4 + d_2d_4 = 0$$

$$\text{Hence } d_3 = d_4 = -\frac{a_2a_3 + b_2b_3}{d_2} = -\frac{1/4 + 1/12}{\sqrt{2/3}} = -\frac{1}{\sqrt{6}}$$

(viii) Normalization condition of  $\psi_3$  gives

$$a_3^2 + b_3^2 + c_3^2 + d_3^2 = 1$$

$$\text{i.e. } \frac{1}{4} + \frac{1}{12} + c_3^2 + \frac{1}{6} = 1$$

$$\text{or } c_3^2 = \frac{1}{2} \quad \text{or } c_3 = +\frac{1}{\sqrt{2}}$$

(ix) For the normalization condition of  $\psi_4$ , we take

$$c_4 = -\frac{1}{\sqrt{2}}$$

Hence the four functions are

$$\begin{aligned}\psi_1 &= \frac{1}{2} \psi_s + \frac{\sqrt{3}}{2} \psi_{p_x} \\ \psi_2 &= \frac{1}{2} \psi_s - \frac{1}{2\sqrt{3}} \psi_{p_x} + \frac{\sqrt{2}}{\sqrt{3}} \psi_{p_z} \\ \psi_3 &= \frac{1}{2} \psi_s - \frac{1}{2\sqrt{3}} \psi_{p_x} + \frac{1}{\sqrt{2}} \psi_{p_y} - \frac{1}{\sqrt{6}} \psi_{p_z} \\ \psi_4 &= \frac{1}{2} \psi_s - \frac{1}{2\sqrt{3}} \psi_{p_x} - \frac{1}{\sqrt{2}} \psi_{p_y} - \frac{1}{\sqrt{6}} \psi_{p_z}\end{aligned}$$

Angle between the Two Orbitals

Utilizing the expression of Eqs (2.13.8) to (2.13.10), we get

$$\begin{aligned}\psi_1 &= \frac{1}{2} + \frac{\sqrt{3}}{2} (\sqrt{3} \sin \theta \cos \varphi) \\ \psi_2 &= \frac{1}{2} - \frac{1}{2\sqrt{3}} (\sqrt{3} \sin \theta \cos \varphi) + \sqrt{\frac{2}{3}} (\sqrt{3} \cos \theta) \\ \psi_3 &= \frac{1}{2} - \frac{1}{2\sqrt{3}} (\sqrt{3} \sin \theta \cos \varphi) + \frac{1}{\sqrt{2}} (\sqrt{3} \sin \theta \sin \varphi) - \frac{1}{\sqrt{6}} (\sqrt{3} \cos \theta) \\ \psi_4 &= \frac{1}{2} - \frac{1}{2\sqrt{3}} (\sqrt{3} \sin \theta \cos \varphi) - \frac{1}{\sqrt{2}} (\sqrt{3} \sin \theta \sin \varphi) - \frac{1}{\sqrt{6}} (\sqrt{3} \cos \theta)\end{aligned}$$

Let  $\psi_1$  have its maximum on x-axis, for  $\theta = 90^\circ$  and  $\varphi = 0^\circ$ . Thus, the relative magnitude of  $\psi_1$  on x-axis is

$$\frac{1}{2} + \frac{3}{2} = 2$$

This may be compared with the value of 1.732 of the  $p_z$  orbital.

We have assumed the function  $\psi_2$  to lie on the xz-plane. We take  $\varphi = 180^\circ$  for this plane. Substituting this value of  $\varphi$  in  $\psi_2$ , we get

$$\psi_2 = \frac{1}{2} + \frac{1}{2} \sin \theta + \sqrt{2} \cos \theta$$

Setting  $d\psi_2/d\theta = 0$ , we get

$$\frac{1}{2} \cos \theta - \sqrt{2} \sin \theta = 0$$

$$\text{or } \tan \theta = \frac{1}{2\sqrt{2}} = \frac{1}{2.828} = 0.354$$

Hence  $\theta = 19^\circ 28'$

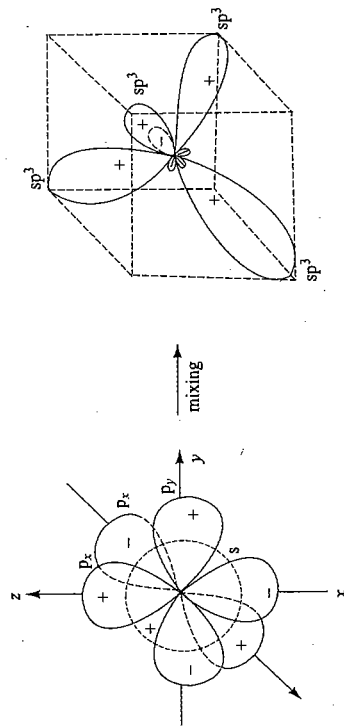


Fig. 2.13.3 Schematic plots of  $sp^3$  hybridization. The correct shape of  $sp^3$  hybrid orbital is shown in Fig. 2.13.4

### Examples

#### Comparison of Hybrid Orbitals

Fig. 2.13.4 Comparison of  $sp$ ,  $sp^2$  and  $sp^3$  hybrid orbitals. The solid, dashed and dotted lines represent  $sp$ ,  $sp^2$  and  $sp^3$  hybrid orbitals respectively

#### Hybrid Orbitals Involving d Orbitals

The hybrid orbitals involving d orbitals have been used in understanding the structure of transition metal complexes. The most common hybrid orbitals of the above types along with their spatial arrangements are given below.

$dsp^2$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Cu}(\text{NH}_4)_4]^{2+}$ , $\text{PdCl}_4^{2-}$
$dsp^3$	Trigonal bipyramidal	$\text{PF}_5$ , $\text{PCl}_5$
$d^2sp^3$	Octahedral	$\text{SF}_6$ , $[\text{Fe}(\text{CN})_6]^{3-}$ , $[\text{Fe}(\text{CN})_6]^{4-}$

Numerous other types of hybridization are possible. Table 2.12.1 gives a brief account of these orbitals.

† See Annexure III for the explanation of  $sp^3$  orbitals shown in Fig. 2.13.3.



Table 2.12.1 Hybrid Orbitals

Coordination number	Shape	Hybridization
2	linear	dp
	bent	$p^2, ds, d^2$
3	trigonal planar	$dp^2, ds^2, d^3$
	unsymmetrical planar	dsp
4	trigonal pyramidal	$p^3, d^2p$
	tetrahedral	$d^3s$
	irregular tetrahedral	$d^2sp, dp^3, d^3p$
5	tetragonal pyramidal	$d^4$
	bipyramidal	$dsp^3, d^3sp$
	tetragonal pyramidal	$d^2sp^2, d^4s, d^2p^3, d^4p$
	pentagonal planar	$d^3p^2$
	pentagonal pyramidal	$d^5$
6	trigonal prismatic	$d^4sp, d^5p$
	trigonal antiprismatic	$d^3p^3$

## 2.14 TRIATOMIC MOLECULES

### General Procedure of Building Molecular Orbitals

In this section, we describe the approximate MO treatment of  $\text{BeH}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  molecules. The first two molecules are linear and the last one is nonlinear.

In general, we can take the linear combination of the valence orbitals of all the three atoms. The coefficients can, as usual, be determined by the variation method. The number of molecular orbitals ( $n$ ) formed will be equal to the number of atomic orbitals ( $n$ ) that are being mixed to form the molecular orbitals. The energies of these molecular orbitals can be worked out by opening the  $n \times n$  secular determinant, equating the resultant expression to zero, and then solving the expression for  $E_s$ . The coefficients in a MO may then be worked out by substituting the corresponding energy in the  $n$  simultaneous linear (secular) equations along with the normalization equation of the molecular orbital. The above calculations can be performed in a very short time with the help of electronic computers. In this section as stated above, we will develop qualitatively the expressions of molecular orbitals and their relative energies by following a few guidelines given below.

### Qualitative Description of Building Molecular Orbitals

- Only those valence atomic orbitals belonging to different atoms will appear in the molecular orbital for which the overlapping is positive. For example, in the linear molecule  $\text{BeH}_2$ , 1s orbitals of hydrogen atoms will have positive overlap with the 2s and  $2p_z$  orbitals of beryllium. Hence, the combination involving either 1s(H) and 2s(Be) or 1s(H) and  $2p_z(\text{Be})$  will appear in the molecular orbital.
- The molecules to be dealt in this section have a general formula of  $\text{AB}_2$ . The LCAO-MO treatment becomes very much simplified by considering first the positive and negative combinations of two higher energy atomic orbitals of B

atoms. For example, in  $\text{BeH}_2$ , we will take the combinations of two 1s orbitals centred on the two hydrogen atoms, i.e.

$$\begin{aligned} \psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)} \\ \psi_{1s(\text{H}_a)} - \psi_{1s(\text{H}_b)} \end{aligned}$$

Note that both the orbitals will have identical coefficients as the two atoms are symmetrically placed around the third atom.

In  $\text{CO}_2$ , we will take the 2p orbitals and not the 2s orbitals as 2p orbital has higher energy than 2s orbital. The latter thus acts as nonbonding orbital.

- The above two combinations are mixed one by one with the proper orbitals of atom A. By the proper orbitals, we mean the matching of the symmetry regarding the signs of lobes of orbital of atom A with that of the combination given above. Thus, the function  $\psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)}$  which carries the same sign in both the lobes will mix only with  $\psi_{2s(\text{A})}$  as the latter carries only one lobe with the positive sign. The combination  $\psi_{1s(\text{H}_a)} - \psi_{1s(\text{H}_b)}$  which carries positive and negative signs over the two lobes will combine only with  $\psi_{2p_z(\text{A})}$  as the latter also carries two lobes with positive and negative signs.

- While considering the signs of lobes in atomic orbitals, we have to consider a coordinate system for the molecule. The lobe pointing towards the increasing direction (shown by arrow) carries a positive sign and that away from the arrow carries a negative sign.

- For each mixing discussed above, we will get two combinations, one by the algebraic addition and the other by algebraic subtraction. For example, for  $\psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)}$  combination with  $\psi_{2s(\text{A})}$ , we will get two wave functions:

$$\begin{aligned} \psi_1 &= C_1 \psi_{2s(\text{A})} + C_2 (\psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)}) \\ \psi_2 &= C_3 \psi_{2s(\text{A})} - C_4 (\psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)}) \end{aligned}$$

To know whether  $\psi_1$  or  $\psi_2$  is bonding, the following procedure is adopted.

- Put the points showing the locations of atoms in the molecule. Draw the atomic orbitals involved in a given molecular orbital along with the correct signs of lobes. Carry out the changes in the signs of lobes of atomic orbital if it is being subtracted. Now if the atomic two lobes of nearby atoms carry the same sign, the molecular orbital is bonding. If it carries opposite signs the orbital is antibonding.

- The boundary surface of the molecular orbital may be derived very easily from the algebraic signs of the nearby lobes and the coefficients  $C_1$  and  $C_2$  in the molecular orbital. In general, the coefficient of more electronegative atom in the bonding molecular orbital has a larger value as compared to that of the lesser electronegative atom. In the antibonding orbital the reverse is true, i.e. the coefficient of the lesser electronegative atom carries the larger value in comparison to that of more electronegative atom. If the coefficient of the atomic orbital is larger, then there occurs an enhancement in the electronic cloud at the involved atom.

We now consider the MO treatment for the above mentioned molecules.



### BERYLLIUM HYDRIDE

#### Geometry of the Molecule

The beryllium hydride is a linear molecule (Fig. 2.14.1). The coordinate system adopted is also shown in Fig. 2.14.1.

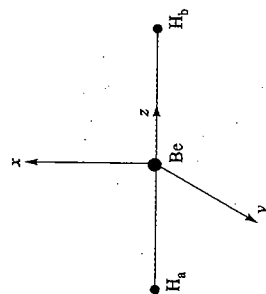


Fig. 2.14.1 The coordinate system of  $\text{BeH}_2$

#### Formation of Different Molecular Orbitals

In beryllium hydride, the valence orbitals  $1s(\text{H}_a)$ ,  $1s(\text{H}_b)$ ,  $2s(\text{Be})$ ,  $2p_x(\text{Be})$ ,  $2p_y(\text{Be})$  and  $2p_z(\text{Be})$  are involved in the formation of molecular orbitals. The various molecular orbitals may be formed as follows.

1. From the  $1s(\text{H}_a)$  and  $1s(\text{H}_b)$  orbitals, the following two group orbitals may be formed.

$$\psi_+ = \psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)} \quad ; \quad \text{symmetrical}$$

$$\psi_- = \psi_{1s(\text{H}_a)} - \psi_{1s(\text{H}_b)} \quad ; \quad \text{antisymmetrical}$$

These two group orbitals are of  $\sigma$  type.

2. Since the group orbital  $\psi_+$  is symmetrical, it may be combined linearly with the symmetrical  $2s$  orbital of beryllium. Since the group orbital  $\psi_-$  is antisymmetrical, it will combine with the antisymmetrical  $2p_z$  orbital of beryllium. Hence, the four molecular orbitals formed from these mixing are as follows.

$$\psi_1 = C_1 \psi_{2s(\text{Be})} + C_2 (\psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)}) \quad (2.14.1)$$

$$\psi_2 = C_3 \psi_{2s(\text{Be})} - C_4 (\psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)}) \quad (2.14.2)$$

$$\psi_3 = C_5 \psi_{2p_z(\text{Be})} + C_6 (\psi_{1s(\text{H}_a)} - \psi_{1s(\text{H}_b)}) \quad (2.14.3)$$

$$\psi_4 = C_7 \psi_{2p_z(\text{Be})} - C_8 (\psi_{1s(\text{H}_a)} - \psi_{1s(\text{H}_b)}) \quad (2.14.4)$$

3. The atomic orbitals  $2p_x(\text{Be})$  and  $2p_y(\text{Be})$  have zero overlap with  $1s(\text{H}_a)$  and  $1s(\text{H}_b)$ . Thus, no mixing between these orbitals takes place. Thus,  $2p_x(\text{Be})$  and  $2p_y(\text{Be})$  orbitals will be nonbonding in nature.

The nature of a molecular orbital may be determined as usual from the signs of nearby lobes of its constituent atomic orbitals. From Fig. 2.14.2, the conclusions drawn are shown in Table 2.14.1.

#### Nature of Molecular Orbitals

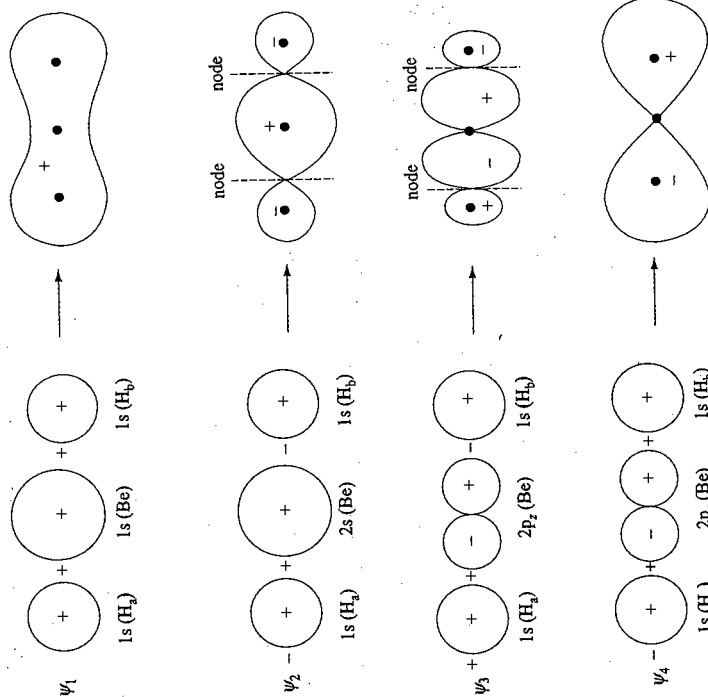


Fig. 2.14.2 Contour diagrams of molecular orbitals (The approximate representation involving only angular function for  $2p$  orbitals is used.)

Table 2.14.1 Nature of Molecular Orbitals of Beryllium Hydride

Molecular orbital	Signs of the nearby lobes	Nature of MO
$\psi_1$	same	bonding
$\psi_2$	different	antibonding
$\psi_3$	different	antibonding
$\psi_4$	same	bonding

A few characteristics of molecular orbitals are shown in Table 2.14.2. In the light of these characteristics, the contour diagrams of molecular orbitals can be drawn. These are shown in Fig. 2.14.2.

#### Contour Diagrams of MO

Table 2.14.2 A Few Characteristics of Molecular Orbitals

Molecular orbital	Nature	Relative values of coefficients <sup>†</sup>	Characteristic	
			Mixing of nearby lobes	Electron density on <sup>‡</sup>
$\psi_1$	bonding	$C_2 > C_1$	Yes	H > Be
$\psi_2$	antibonding	$C_3 > C_4$	No	Be > H
$\psi_3$	antibonding	$C_3 > C_6$	No	Be > H
$\psi_4$	bonding	$C_5 > C_7$	Yes	H > Be

<sup>†</sup> In bonding orbital, the coefficient of more electronegative atom will be larger than that of less electronegative atom. In antibonding orbital, the reverse is true.

<sup>‡</sup> The electron density on A > B implies that the function  $\psi$  will have larger value nearly the atom A as compared to the atom B.

The following factors help deciding the relative orbital energies in beryllium hydride (Fig. 2.14.3).

1. Since H is more electronegative than Be, the 1s orbitals of hydrogen atoms are more stable than 2s and 2p orbitals of Be.
2. The group orbital  $\psi_4$  is of bonding nature. Hence, its energy will be smaller than those of 1s(H) orbitals.
3. The group orbital  $\psi_-$  is of antibonding nature. Hence, its energy will be greater than that of 1s(H) orbital.
4. The bonding molecular orbital  $\psi_1$  will be more stable than the more stable constituent orbital, i.e.  $\psi_+$ .
5. The antibonding molecular orbital  $\psi_2$  will be less stable than the lesser stable constituent orbital, i.e. 2s(Be).
6. The antibonding molecular orbital  $\psi_3$  will be less stable than the lesser stable constituent orbital, i.e. 2p<sub>x</sub>(Be).
7. The bonding molecular orbital  $\psi_4$  will be more stable than the more stable constituent orbital, i.e.  $\psi_-$ .
8. The orbital  $\psi_1$  will be more stable than  $\psi_4$  as the overlapping of 1s(H) and 2s(Be) is more than that of 1s(H) and 2p<sub>x</sub>(Be).
9. The orbital  $\psi_3$  will be less stable than  $\psi_2$  as the energy of 2p(Be) orbital is larger than that of 2s(Be).
10. The atomic orbitals 2p<sub>x</sub>(Be) and 2p<sub>y</sub>(Be) will act as nonbonding  $\pi$  molecular orbitals. Their energies will remain unaffected.

Keeping in mind the above factors, the relative orbital energies in BeH<sub>2</sub> is shown in Fig. 2.14.3. Since there are four valence electrons (two from Be and one from each H), the electronic configuration of BeH<sub>2</sub> is  $(\psi_1)^2(\psi_4)^2$

### Example 2.14.1

The two lowest molecular orbitals of the molecule H<sub>a</sub>—Be—H<sub>b</sub> are given by

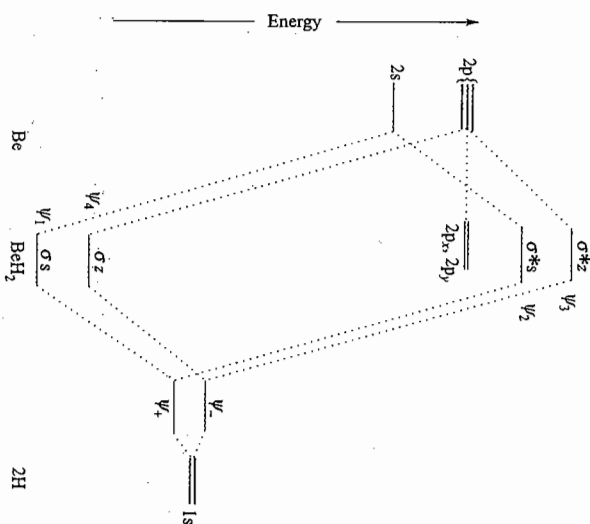
$$\psi_1 = C_1 \psi_{1s(H_a)} + C_2 \psi_{2s(Be)} + C_3 \psi_{1s(H_b)}$$

$$\psi_2 = C_4 \psi_{1s(H_a)} - C_5 \psi_{2p_z(Be)} - C_6 \psi_{1s(H_b)}$$

with  $C_1 = 0.59$  and  $C_4 = 0.63$ . Evaluate the charge densities of Be and H atoms.

Fig. 2.14.3 Relative orbital energy of BeH<sub>2</sub>

### Solution



Based on the symmetry of BeH<sub>2</sub>, we expect that

$$C_1 = C_3 \text{ and } C_4 = C_6$$

Under the zero-overlap approximation, we will have

$$C_1^2 + C_2^2 + C_3^2 = 1 \Rightarrow 2C_1^2 + C_2^2 = 1 \Rightarrow C_2 = \sqrt{1-2C_1^2}$$

$$\Rightarrow C_2 = \sqrt{1-2 \times 0.59^2} = 0.55$$

$$\text{and } C_1^2 + C_2^2 + C_3^2 = 1 \Rightarrow 2C_1^2 + C_3^2 = 1 \Rightarrow C_3 = \sqrt{1-2C_1^2}$$

$$\Rightarrow C_3 = \sqrt{1-2 \times 0.63^2} = 0.45$$

Since the electronic configuration of BeH<sub>2</sub> is  $(\psi_1)^2(\psi_4)^2$ , we will have

$$\text{Charge on H}_a \text{ (or H}_b\text{)} = 2 \times 0.59^2 + 2 \times 0.63^2 = 1.49$$

$$\text{Charge on Be} = 2 \times 0.55^2 + 2 \times 0.45^2 = 1.01$$

Multiplication by 2 in each term in the above two expressions is due to the fact that each of the two occupied molecular orbital contains 2 electrons.

### Localized Molecular Orbitals of BeH<sub>2</sub>

It is customary to visualize the molecule of BeH<sub>2</sub> in terms of the localized two-electron bonds in between each of the two Be—H direction. Since the molecule is linear, each of the Be—H bond is considered to be formed as a result of overlapping between sp hybrid orbital of Be and 1s orbital of H as shown in Fig. 2.14.4. The other two p orbitals of Be atoms, which lie perpendicular to the molecular axis, are not involved in the bonding and hence they constitute a doubly degenerate nonbonding orbitals of the molecule.

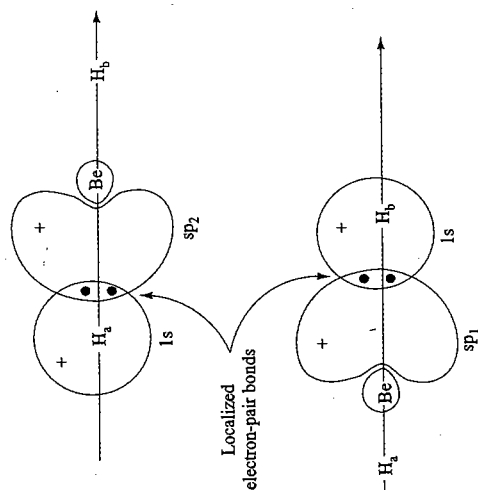


Fig. 2.14.4 Localized bonds in  $\text{BeH}_2$

The two  $sp$  hybrid orbitals of Be atom are:

$$\psi_{sp_1}(\text{Be}) = \frac{1}{\sqrt{2}} (\psi_{2s}(\text{Be}) + \psi_{2p_z}(\text{Be}))$$

$$\psi_{sp_2}(\text{Be}) = \frac{1}{\sqrt{2}} (\psi_{2s}(\text{Be}) - \psi_{2p_z}(\text{Be}))$$

The molecular orbitals describing the localized Be—H bonds are:

$$\psi_{1, \text{loc}} = C_1' \psi_{sp_1}(\text{Be}) + C_2' \psi_{1s}(\text{H}_b) \quad (2.14.5)$$

$$\psi_{2, \text{loc}} = C_1' \psi_{sp_2}(\text{Be}) + C_2' \psi_{1s}(\text{H}_a) \quad (2.14.6)$$

where the subscript loc stands for the term localized. Substituting the expressions of  $\psi_{sp_1}(\text{Be})$  and  $\psi_{sp_2}(\text{Be})$ , we get

$$\psi_{1, \text{loc}} = C_1'' (\psi_{2s}(\text{Be}) + \psi_{2p_z}(\text{Be})) + C_2' \psi_{1s}(\text{H}_b)$$

$$\psi_{2, \text{loc}} = C_1'' (\psi_{2s}(\text{Be}) - \psi_{2p_z}(\text{Be})) + C_2' \psi_{1s}(\text{H}_a)$$

While describing the excitation of an electron, the above treatment of localized orbitals is not useful since it is not possible to associate the electron as coming from one Be—H link or the other. The two links are completely identical and are indistinguishable. However, this difficulty can be overcome by converting localized molecular orbitals into nonlocalized orbitals. This is achieved by taking 'positive' and 'negative' combinations of  $\psi_{1, \text{loc}}$  and  $\psi_{2, \text{loc}}$  as shown in the following:

#### Conversion of Localized MO into Nonlocalized MO and vice versa

$$\psi_1 = \psi_{1, \text{loc}} + \psi_{2, \text{loc}}$$

$$\psi_4 = \psi_{1, \text{loc}} - \psi_{2, \text{loc}}$$

Substituting the expression of  $\psi_{1, \text{loc}}$  and  $\psi_{2, \text{loc}}$ , we get

$$\psi_1 = C_1'' \psi_{2s}(\text{Be}) + C_2' (\psi_{1s}(\text{H}_a) + \psi_{1s}(\text{H}_b))$$

$$\psi_4 = C_1'' \psi_{2p_z}(\text{Be}) - C_2' (\psi_{1s}(\text{H}_a) - \psi_{1s}(\text{H}_b))$$

The functions  $\psi_1$  and  $\psi_4$  are, in fact, the same as described earlier (Eqs 2.14.1 and 2.14.4). Thus, from the two localized orbitals, we have got two nonlocalized molecular orbitals.

The above treatment of constructing two nonlocalized molecular orbitals out of two localized orbitals can be reversed, i.e. out of two nonlocalized orbitals, we can construct two localized orbitals by simply taking the 'positive' and 'negative' combinations of  $\psi_1$  and  $\psi_4$ . If we do so, we get back the functions  $\psi_{1, \text{loc}}$  and  $\psi_{2, \text{loc}}$ .

The antibonding counterparts of localized bonding molecular orbitals are

$$\psi_{1, \text{loc}}' = C_1' \psi_{sp_1}(\text{Be}) - C_2' \psi_{1s}(\text{H}_b)$$

$$\psi_{2, \text{loc}}' = C_1' \psi_{sp_2}(\text{Be}) - C_2' \psi_{1s}(\text{H}_a)$$

The 'positive' and 'negative' combinations of the above two localized molecular orbitals generate the two nonlocalized antibonding orbitals  $\psi_2$  and  $\psi_3$ , respectively.

$$\psi_2 = C_1' \psi_{2s}(\text{Be}) - C_2' (\psi_{1s}(\text{H}_a) + \psi_{1s}(\text{H}_b))$$

$$\psi_3 = C_1' \psi_{2p_z}(\text{Be}) + C_2' (\psi_{1s}(\text{H}_a) - \psi_{1s}(\text{H}_b))$$

The schematic construction of correlation diagram may be carried out by following the steps given below.

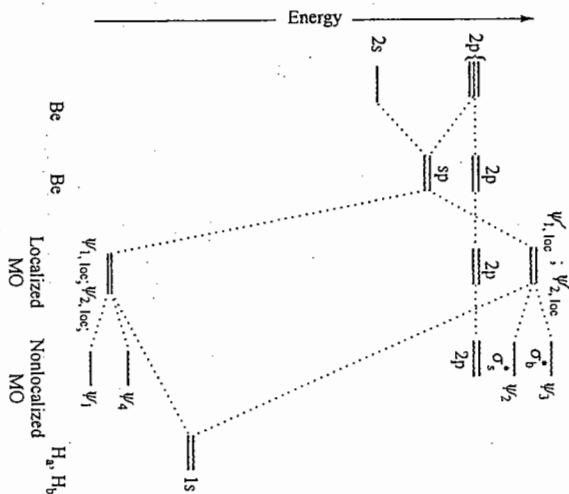
1. Depict the relative energies of atomic orbitals of Be and H atoms. Since H is more electronegative than Be, the 1s orbitals of hydrogen atoms are more stable than 2s and 2p orbitals of Be.
2. Depict the formation of  $sp$  hybrid orbitals of Be. The energies of hybrid orbitals will be greater than that of 2s orbital but smaller than that of 2p orbital.
3. Depict the formation of localized molecular orbitals. There will be two bonding (degenerate) and two antibonding (degenerate) orbitals.

Figure 2.14.5 exhibits the expected correlation diagram. Since  $\text{BeH}_2$  has four valence electrons, its configuration is

$$(\psi_{1, \text{loc}})^2 (\psi_{2, \text{loc}})^2$$

Figure 2.14.5 also exhibits the change in energies of localized molecular orbitals when they are converted into nonlocalized molecular orbitals.

Fig. 2.14.5 Correlation diagram for localized orbitals of  $\text{BeH}_2$



### Comment on Hybridization

As described in Section 1.12, the eigenfunction of a polyelectronic atom is antisymmetric with respect to the exchange of the coordinates of any two electrons, and can be expressed as a Slater determinant whose elements are the various occupied spin atomic orbitals. The same is applicable to a polyelectronic molecule with the replacement of spin atomic orbitals by the spin molecular orbitals. For example, the total molecular wave function of  $\text{BeH}_2$ , which contains four valence electrons can be written as

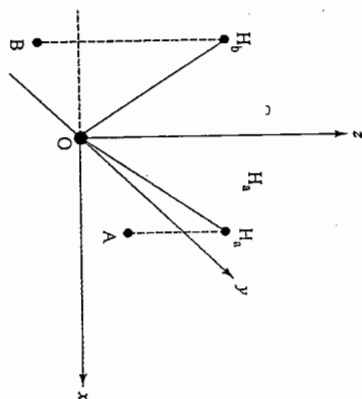
$$\psi = \frac{1}{\sqrt{4!}} \begin{vmatrix} \psi_1(1) & \bar{\psi}_1(1) & \psi_4(1) & \bar{\psi}_4(1) \\ \psi_1(2) & \bar{\psi}_1(2) & \psi_4(2) & \bar{\psi}_4(2) \\ \psi_1(3) & \bar{\psi}_1(3) & \psi_4(3) & \bar{\psi}_4(3) \\ \psi_1(4) & \bar{\psi}_1(4) & \psi_4(4) & \bar{\psi}_4(4) \end{vmatrix}$$

As described in Section 1.12, the replacement of wave function, say  $\psi$ , by a linear combination  $\psi_1 \pm \psi_2$  does not change the overall wave function, but such a replacement in the present case helps visualizing  $\text{BeH}_2$  as its classical structural formula representing the two bonds between Be and H atoms. It may be mentioned here that the concept of hybrid orbitals follows from molecular geometry and not vice-versa, since the choice of appropriate combination of molecular wave functions representing the required hybrid orbitals from the large number of combinations can be identified only when the molecular geometry is known, i.e., knowing the molecular geometry, one can identify the hybrid orbitals, by replacing the initial set of molecular orbitals by a set of localized molecular orbitals. Since this mathematical substitution does not change the overall molecular wave function, atomic orbital hybridization cannot be regarded as a physical phenomenon.

### WATER

The molecule of water is nonlinear with HOH bond angle equal to  $105^\circ$ . The coordinate system of  $\text{H}_2\text{O}$  is given in Fig. 2.14.6.

Fig. 2.14.6 Coordinate system of  $\text{H}_2\text{O}$ . Points A and B are the projections of atoms  $\text{H}_a$  and  $\text{H}_b$  on the xy-plane



The proper combinations of bonding and antibonding molecular orbitals of 2H atoms are

$$\psi_+ = \psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)} \quad \text{and} \quad \psi_- = \psi_{1s(\text{H}_a)} - \psi_{1s(\text{H}_b)}$$

The valence orbitals of oxygen are 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub>. Their combinations with  $\psi_+$  and  $\psi_-$  are as follows.

1. From Fig. 2.14.7, where the overlapping of 1s(H) orbitals with 2p<sub>z</sub>(O) orbital is shown, it may be concluded that the proper combination of two hydrogen atoms that can combine with 2p<sub>z</sub> orbital of oxygen is  $1s(\text{H}_a) + 1s(\text{H}_b)$ . Besides this,  $1s(\text{H}_a) + 1s(\text{H}_b)$  group orbital will also have positive overlap with 2s orbital of oxygen. Thus, we may consider the formation of three nonlocalized molecular orbitals by mixing three atomic orbitals,  $\psi_{2s(\text{O})}$ ,  $\psi_{2p_z(\text{O})}$  and  $\psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)}$ , i.e.

$$\psi_{1,2,3} = C_1 \psi_{2s(\text{O})} + C_2 \psi_{2p_z(\text{O})} + C_3 (\psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)}) \quad (2.14.7)$$

2. From Fig. 2.14.8, we may conclude that the proper combination of two hydrogen atoms that can combine with 2p<sub>x</sub> or/and 2p<sub>y</sub> orbitals of oxygen is  $1s(\text{H}_a) - 1s(\text{H}_b)$ . In order to have more effective overlapping, we form first two hybrid orbitals out of 2p<sub>x</sub>(O) and 2p<sub>y</sub>(O) orbitals. These are

$$\psi'_+ = \psi_{2p_x(\text{O})} + \psi_{2p_y(\text{O})} \quad \text{and} \quad \psi'_- = \psi_{2p_x(\text{O})} - \psi_{2p_y(\text{O})}$$

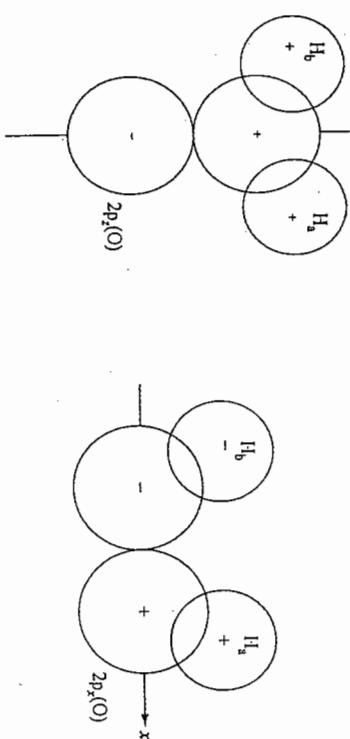


Fig. 2.14.7 Overlapping of group orbital  $\psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)}$  with  $\psi_{2p_z(\text{O})}$

Fig. 2.14.8 Overlapping of group orbital  $\psi_{1s(\text{H}_a)} - \psi_{1s(\text{H}_b)}$  with  $\psi_{2p_x(\text{O})}$

The schematic shapes of  $\psi_+$  and  $\psi_-$  are shown in Fig. 2.14.9.

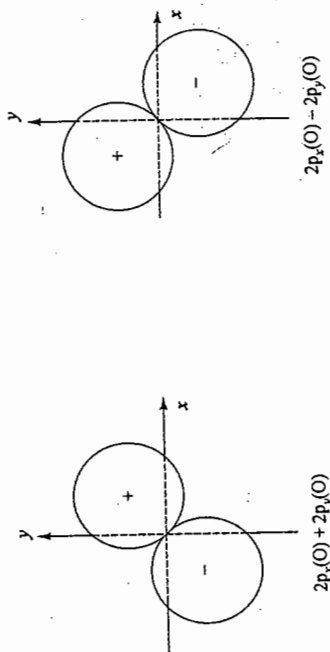


Fig. 2.14.9  
 $\psi_{2p_z}(O) + \psi_{2p_z}(O)$  and  
 $\psi_{2p_z}(O) - \psi_{2p_z}(O)$   
orbitals

From Figs 2.14.6 and 2.14.9, it is obvious that  $\psi_{1s(H_a)} - \psi_{1s(H_b)}$  will have positive overlap with  $\psi_{2p_x}(O) + \psi_{2p_y}(O)$ , whereas the overlap with  $\psi_{2p_z}(O) - \psi_{2p_y}(O)$  is zero. Thus, we construct two molecular orbitals out of the combinations of  $\{\psi_{1s(H_a)} - \psi_{1s(H_b)}\}$  and  $\{\psi_{2p_x}(O) + \psi_{2p_y}(O)\}$  as follows:

$$\psi_{4,5} = C_4 (\psi_{2p_x}(O) + \psi_{2p_y}(O)) + C_5 (\psi_{1s(H_a)} - \psi_{1s(H_b)}) \quad (2.14.8)$$

The orbital  $\psi_{2p_z}(O) - \psi_{2p_y}(O)$  will act as a nonbonding molecular orbital.

The following factors help deciding the relative orbital energies in  $H_2O$ .

1. Since oxygen is more electronegative than hydrogen, the 2s and 2p orbitals of oxygen are more stable than 1s hydrogen orbital.
2. Out of the three orbitals  $\psi_1$ ,  $\psi_2$  and  $\psi_3$ , one will be strongly bonding (say,  $\psi_1$ ), second will be bonding but near to nonbonding (say,  $\psi_2$ ) and the third will be antibonding (say,  $\psi_3$ ).
3. Out of the orbitals  $\psi_4$  and  $\psi_5$ , one will be bonding (say,  $\psi_4$ ) and the other will be antibonding (say,  $\psi_5$ ).
4. The orbital  $\psi_1$  will be more stable than  $\psi_4$ .
5. The orbital  $\psi_4$  will be more stable than  $\psi_2$ .
6. In the antibonding orbitals,  $\psi_5$  is expected to be less stable than  $\psi_3$ .
7. The orbital  $\psi_- = \psi_{2p_x}(O) - \psi_{2p_y}(O)$  is nonbonding. Hence, its energy is the same as that of pure p orbital.

With the above facts, we may draw the correlation diagram depicting the relative order of orbital energies as shown in Fig. 2.14.10. Since there are eight valence electrons (six from oxygen and one from each hydrogen), the electronic configuration of  $H_2O$  is

$$(\psi_1)^2 (\psi_4)^2 (\psi_2)^2 (\psi_-)^2$$

The molecule will be diamagnetic in nature.

Fig. 2.14.10 Correlation  
diagram of  $H_2O$

### Localized Molecular Orbitals of $H_2O$

The formation of localized molecular orbitals in water is explained from the following two view points:

1. The two OH bonds are formed as a result of overlapping between 2p oxygen orbitals and 1s hydrogen orbitals (Fig. 2.14.11). Thus, we have

$$\psi'_1 = C'_1 \psi_{2p_x}(O) + C'_2 \psi_{1s(H_a)} \quad \text{and} \quad \psi'_2 = C'_1 \psi_{2p_y}(O) + C'_2 \psi_{1s(H_b)}$$

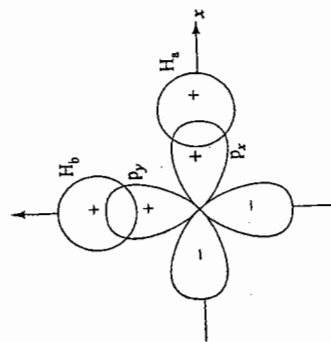
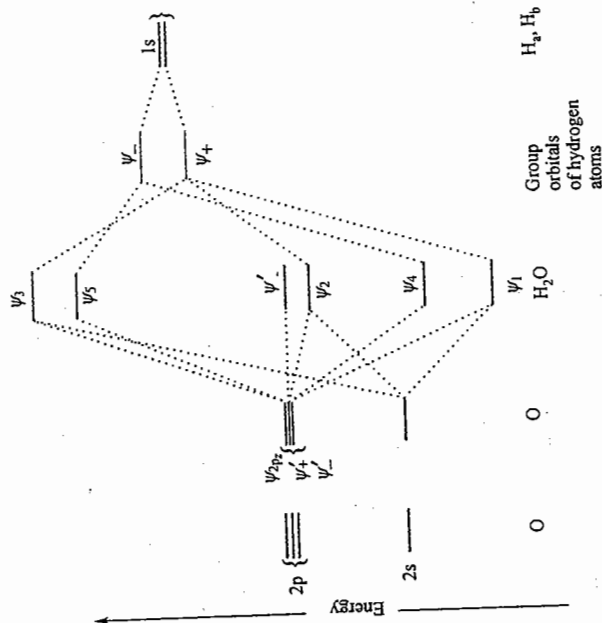


Fig. 2.14.11  
Overlapping of  $2p_x$   
and  $2p_y$  orbitals of  
oxygen with 1s orbital  
of hydrogen

The expected bond angle of  $90^\circ$  between the two OH bonds is expanded a little due to the repulsion of two protons. This model of  $H_2O$  neglects the two lone pairs of electrons in 2s and one of the 2p orbitals of oxygen.

2. Since water molecule contains eight valence electrons, the most stable structure would be the one where these electrons stay as far apart from each other as possible. This is achieved by visualizing the valence orbitals of oxygen in the



$sp^3$  hybrid state where the four equivalent orbitals point towards the corner of a regular tetrahedron (Fig. 2.14.12).

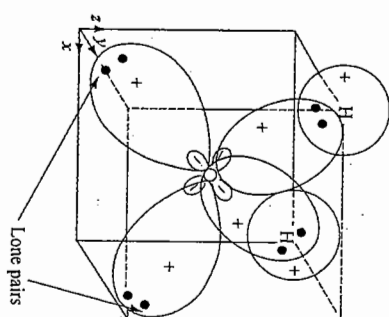


Fig. 2.14.12 Tetrahedral model of  $H_2O$

The two OH bonds in water are thus formed by overlapping between the two  $sp^3$  hybrid orbitals of oxygen and 1s orbitals of hydrogen atoms. For the ion  $O^{2-}$  the arrangement of four lone pairs is expected to be perfectly tetrahedral, but when two of these orbitals are utilized by two protons, this arrangement is slightly disturbed due to the shifting of electron pairs away from oxygen. Consequently, the angle of  $109^\circ 28'$  between the two orbitals of  $O^{2-}$  is changed to  $105^\circ$  in water, owing to the expansion of the electronic cloud by the two protons. The expansion of electronic cloud means the OH bonds acquire a little more of 2p character.

Mathematically, the four  $sp^3$  hybrid orbitals of oxygen are given by the expressions

$$\begin{aligned}\psi_{sp^3_1}(O) &= \frac{1}{2}\psi_{2s}(O) + \frac{1}{2}\psi_{2p_x}(O) + \frac{1}{2}\psi_{2p_y}(O) + \frac{1}{2}\psi_{2p_z}(O) \\ \psi_{sp^3_2}(O) &= \frac{1}{2}\psi_{2s}(O) - \frac{1}{2}\psi_{2p_x}(O) - \frac{1}{2}\psi_{2p_y}(O) + \frac{1}{2}\psi_{2p_z}(O) \\ \psi_{sp^3_3}(O) &= \frac{1}{2}\psi_{2s}(O) - \frac{1}{2}\psi_{2p_x}(O) + \frac{1}{2}\psi_{2p_y}(O) - \frac{1}{2}\psi_{2p_z}(O) \\ \psi_{sp^3_4}(O) &= \frac{1}{2}\psi_{2s}(O) + \frac{1}{2}\psi_{2p_x}(O) - \frac{1}{2}\psi_{2p_y}(O) - \frac{1}{2}\psi_{2p_z}(O)\end{aligned}$$

Considering the formation of the two localized molecular orbitals from  $\psi_{sp^3_1}$  and  $\psi_{sp^3_2}$ , we have

$$\psi_{1, loc} = C'_1\psi_{sp^3_1}(O) + C'_2\psi_{1s(H_a)} \quad (2.14.9)$$

$$\psi_{2, loc} = C'_1\psi_{sp^3_2}(O) + C'_2\psi_{1s(H_b)} \quad (2.14.10)$$

i.e.

$$\psi_{1, loc} = C'_1\left(\frac{1}{2}\psi_{2s}(O) + \frac{1}{2}\psi_{2p_x}(O) + \frac{1}{2}\psi_{2p_y}(O) + \frac{1}{2}\psi_{2p_z}(O)\right) + C'_2\psi_{1s(H_a)}$$

While describing the excitation of an electron, the above treatment of localized orbitals is not useful since it is not possible to associate the electron as coming from one OH link or the other. The two links are completely identical and are indistinguishable. However, this difficulty can be overcome by converting localized molecular orbitals into nonlocalized orbitals. This is achieved by taking 'positive' and 'negative' combinations of  $\psi_{1, loc}$  and  $\psi_{2, loc}$  as follows.

$\psi_1 = \psi_{1, loc} + \psi_{2, loc}$  and  $\psi_4 = \psi_{1, loc} - \psi_{2, loc}$   
Substituting the expressions of  $\psi_{1, loc}$  and  $\psi_{2, loc}$  we get

$$\psi_1 = C'_1(\psi_{2s}(O) + \psi_{2p_z}(O)) + C'_2(\psi_{1s(H_a)} + \psi_{1s(H_b)})$$

The functions  $\psi_1$  and  $\psi_4$  are, in fact, the same as described earlier (Eqs 2.14.7 and 2.14.8) provided, we have

$$C_1 = C_2 = C_4 = C'_1 \text{ and } C_3 = C_5 = C'_2$$

The above treatment of constructing two nonlocalized molecular orbitals out of two localized orbitals can be reversed, i.e. out of two nonlocalized orbitals, we can construct two localized orbitals by simply taking the 'positive' and 'negative' combinations of  $\psi_1$  and  $\psi_4$ . If we do so, we get back the functions  $\psi_{1, loc}$  and  $\psi_{2, loc}$  respectively.

The schematic construction of correlation diagram may be carried out by following the steps given below.

1. Depict the relative energies of atomic orbitals of O and H atoms. Since oxygen is more electronegative than hydrogen, the 2s and 2p orbitals of oxygen are more stable than 1s hydrogen orbital.
2. Depict the  $sp^3$  hybridization of oxygen orbitals. The energies of  $sp^3$  hybrid orbitals will be greater than that of 2s orbital but smaller than those of 2p orbitals.
3. Depict the formation of localized molecular orbitals. There will be two bonding (degenerate) and two antibonding (degenerate) orbitals.

Figure 2.14.13 exhibits the expected correlation diagram. Since  $H_2O$  has eight valence electrons, its configuration is  $(\psi_{1, loc})^2(\psi_{2, loc})^2(\psi_{sp^3_3})^2(\psi_{sp^3_4})^2$ . Figure 2.14.13 also exhibits the change in energies of localized molecular orbitals when they are converted into nonlocalized molecular orbitals.

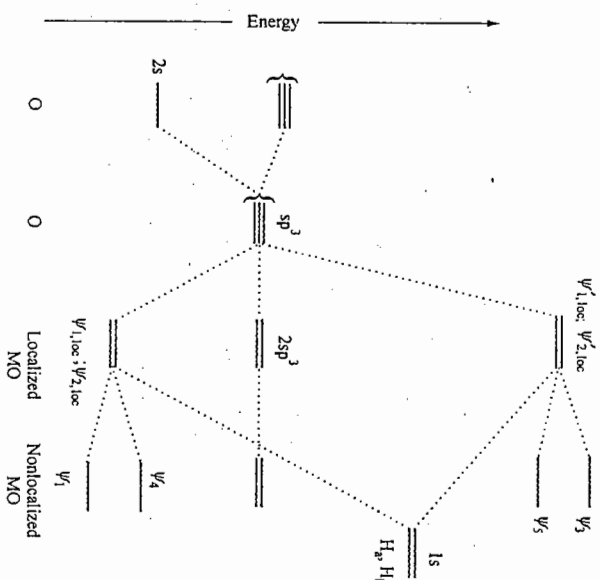


Fig. 2.14.13 Correlation diagram of  $H_2O$

### CARBON DIOXIDE

The carbon dioxide is a linear molecule (Fig. 2.14.14). The coordinate system adopted is also shown in Fig. 2.14.14.

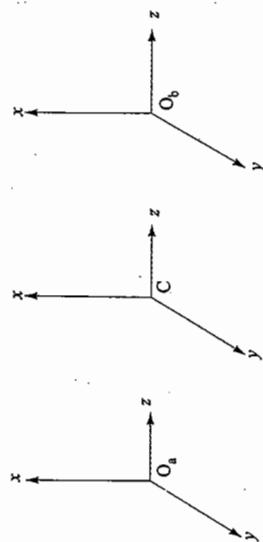


Fig. 2.14.14 The coordinate system of  $\text{CO}_2$

### Formation of Different Molecular Orbitals

In carbon dioxide, all the three atoms have 2s and 2p valence orbitals and thus will be involved in the formation of molecular orbitals. The various molecular orbitals may be formed as follows.

1. Since the energies of  $2s(\text{O}_a)$  and  $2s(\text{O}_b)$  orbitals are far off from the energies of other orbitals, the mixing of these two orbitals with other orbitals will be small and thus may be treated as the nonbonding orbitals.
2. Of the six 2p orbitals of the two oxygen atoms, the following six group orbitals may be formed.

$$\psi_{1-} = \psi_{2p_z}(\text{O}_a) - \psi_{2p_z}(\text{O}_b); \quad \text{symmetrical}$$

$$\psi_{1+} = \psi_{2p_z}(\text{O}_a) + \psi_{2p_z}(\text{O}_b); \quad \text{antisymmetrical}$$

$$\psi_{2+} = \psi_{2p_x}(\text{O}_a) + \psi_{2p_x}(\text{O}_b); \quad \text{antisymmetrical}$$

$$\psi_{2-} = \psi_{2p_x}(\text{O}_a) - \psi_{2p_x}(\text{O}_b); \quad \text{symmetrical}$$

$$\psi_{3+} = \psi_{2p_y}(\text{O}_a) + \psi_{2p_y}(\text{O}_b); \quad \text{antisymmetrical}$$

$$\psi_{3-} = \psi_{2p_y}(\text{O}_a) - \psi_{2p_y}(\text{O}_b); \quad \text{symmetrical}$$

The group orbitals  $\psi_{1-}$  and  $\psi_{1+}$  are of  $\sigma$  type whereas  $\psi_{2-}$ ,  $\psi_{2+}$ ,  $\psi_{3-}$  and  $\psi_{3+}$  are of  $\pi$  type.

3. Since the group orbital  $\psi_{1-}$  is symmetrical, it may be combined linearly with the symmetrical 2s orbital of carbon. The group orbital  $\psi_{1+}$  is antisymmetrical, it will combine with the antisymmetrical  $2p_z$  orbital of carbon.

Hence, the four molecular orbitals formed from these mixing are as follows.

$$\psi_1 = C_1 \psi_{2s}(\text{C}) + C_2 (\psi_{2p_z}(\text{O}_a) - \psi_{2p_z}(\text{O}_b)) \quad (2.14.13)$$

$$\psi_2 = C_3 \psi_{2s}(\text{C}) - C_4 (\psi_{2p_z}(\text{O}_a) - \psi_{2p_z}(\text{O}_b)) \quad (2.14.14)$$

$$\psi_3 = C_5 \psi_{2p_z}(\text{C}) + C_6 (\psi_{2p_z}(\text{O}_a) + \psi_{2p_z}(\text{O}_b)) \quad (2.14.15)$$

$$\psi_4 = C_7 \psi_{2p_z}(\text{C}) - C_8 (\psi_{2p_z}(\text{O}_a) + \psi_{2p_z}(\text{O}_b)) \quad (2.14.16)$$

4. The group orbitals  $\psi_{2+}$  and  $\psi_{3+}$  will have positive overlap with  $2p_x$  and  $2p_y$  orbitals of carbon, respectively. Hence, their linear combinations will result into the following four  $\pi$ -orbitals.

$$\psi_5 = C_9 \psi_{2p_x}(\text{C}) + C_{10} (\psi_{2p_x}(\text{O}_a) + \psi_{2p_x}(\text{O}_b)) \quad (2.14.17)$$

$$\psi_6 = C_{11} \psi_{2p_x}(\text{C}) - C_{12} (\psi_{2p_x}(\text{O}_a) + \psi_{2p_x}(\text{O}_b)) \quad (2.14.18)$$

$$\psi_7 = C_{13} \psi_{2p_y}(\text{C}) + C_{14} (\psi_{2p_y}(\text{O}_a) + \psi_{2p_y}(\text{O}_b)) \quad (2.14.19)$$

$$\psi_8 = C_{15} \psi_{2p_y}(\text{C}) - C_{16} (\psi_{2p_y}(\text{O}_a) + \psi_{2p_y}(\text{O}_b)) \quad (2.14.20)$$

Since the designation of  $x$ - and  $y$ -direction is arbitrary, the molecular orbitals  $\psi_5$  and  $\psi_7$ , and  $\psi_6$  and  $\psi_8$  will constitute a degenerate set with the corresponding coefficients equal in magnitude.

5. The group orbitals  $\psi_{2-}$  and  $\psi_{3-}$  will have zero overlap with  $2p_x$  and  $2p_y$  orbitals of carbon, and thus, will not enter into any combination.

The nature of a molecular orbital may be determined as usual from the signs of nearby lobes of its constituent atomic orbitals. From Fig. 2.14.15, the conclusions drawn are shown in Table 2.14.3.

Table 2.14.3 Nature of Molecular Orbitals

Molecular orbital	Signs of the nearby lobes	Nature of MO
$\psi_1$	same	bonding
$\psi_2$	different	antibonding
$\psi_3$	different	antibonding
$\psi_4$	same	bonding
$\psi_5, \psi_7$	same	bonding
$\psi_6, \psi_8$	different	antibonding

### Contour Diagrams of Molecular Orbitals

A few characteristics of molecular orbitals are shown in Table 2.14.4. In the light of these characteristics, the contour diagrams of molecular orbitals can be drawn and are shown in Fig. 2.14.15.



Fig. 2.14.15 Contour diagrams of molecular orbitals (The approximate representation involving angular functions for 2p orbitals is used.)

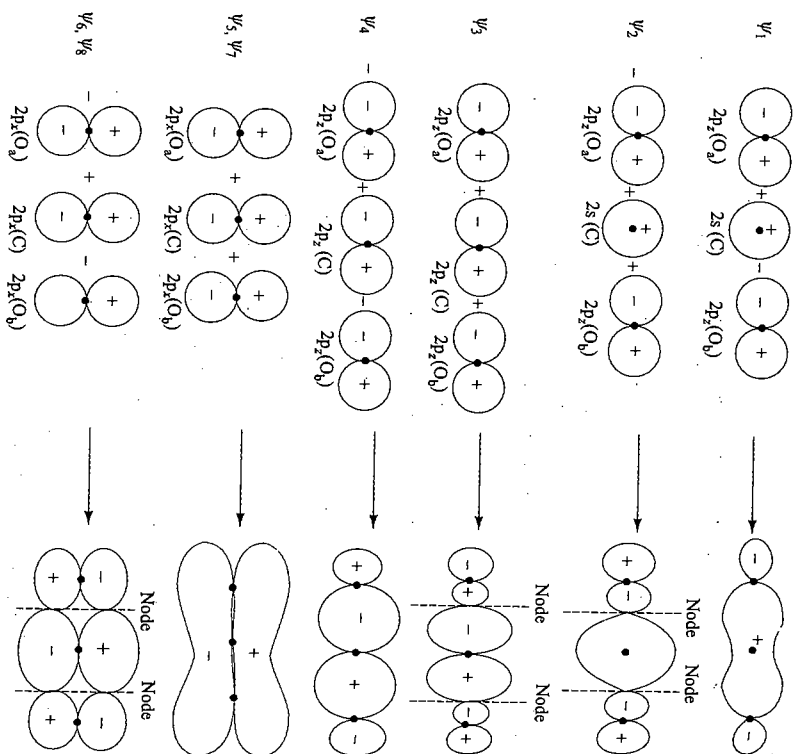


Table 2.14.4 Characteristics of Molecular Orbitals of Carbon Dioxide

Molecular orbital	Nature	Relative values of coefficients <sup>†</sup>	Characteristics	
			Merging of nearby lobes	Electron density on <sup>‡</sup>
$\psi_1$	bonding	$C_2 > C_1$	Yes	$O > C$
$\psi_2$	antibonding	$C_3 > C_4$	No	$C > O$
$\psi_3$	antibonding	$C_5 > C_6$	No	$C > O$
$\psi_4$	bonding	$C_8 > C_7$	Yes	$O > C$
$\psi_5, \psi_6$	bonding	$C_{10} > C_9$	Yes	$O > C$
$\psi_7, \psi_8$	antibonding	$C_{14} > C_{13}$ $C_{11} > C_{12}$ $C_{15} > C_{16}$	No	$C > O$

<sup>†</sup> In bonding orbital, the coefficient of more electronegative atom will be larger than that of the less electronegative atom. In antibonding orbital, the reverse is true.

<sup>‡</sup> The electron density on  $A > B$  implies that the function  $\psi$  will have larger value nearby the atom  $A$  as compared to that of the atom  $B$ .

### Relative Energies of Molecular Orbitals

The following factors help deciding the relative orbital energies in carbon dioxide (Fig. 2.14.16).

1. Since oxygen is more electronegative than carbon, the orbitals 2s and 2p of oxygen are expected to be more stable than the corresponding orbitals of carbon.
2. The 2p orbitals of oxygen atoms are less stable than 2s orbital of carbon (orbital energies correspond to:  $2s(C) = -157 \times 10^3 \text{ cm}^{-1}$ ,  $2p(C) = -86 \times 10^3 \text{ cm}^{-1}$ ;  $2s(O) = -261 \times 10^3 \text{ cm}^{-1}$  and  $2p(O) = -128 \times 10^3 \text{ cm}^{-1}$ ).
3. The group orbitals  $\psi_{1+}$ ,  $\psi_{2+}$  and  $\psi_{3+}$  are of bonding nature. Hence, their energies will be smaller than those of 2p(O) orbitals. The orbital  $\psi_{1-}$  is expected to be more stable than the degenerate orbitals  $\psi_{2-}$  and  $\psi_{3-}$ , as lateral overlapping is larger than the side-way overlapping.
4. The group orbitals  $\psi_{1+}$ ,  $\psi_{2-}$  and  $\psi_{3-}$  are of antibonding nature. Hence, their energies will be greater than those of 2p(O) orbitals. The orbital  $\psi_{1+}$  will be less stable than the degenerate orbitals  $\psi_{2-}$  and  $\psi_{3-}$ .
5. The molecular orbital  $\psi_1$  being a bonding orbital will be more stable than the more stable constituent atomic orbital, i.e. 2s(C).
6. The molecular orbital  $\psi_2$  being an antibonding orbital will be less stable than the lesser stable constituent orbital, i.e.  $\psi_{1-}$ .
7. The molecular orbital  $\psi_3$  being an antibonding orbital will be less stable than the lesser stable constituent orbital, i.e. 2p<sub>x</sub>(C). The orbital  $\psi_5$  is expected to have larger energy than the orbital  $\psi_6$  as 2p(C) has much larger energy than that of 2s(C).
8. The molecular orbital  $\psi_4$  being a bonding orbital will be more stable than the more stable constituent orbital, i.e.  $\psi_{1+}$ .
9. The molecular orbital  $\psi_4$  will be even less stable than  $\psi_6$  as the overlapping between 2p<sub>x</sub>(O) and 2p<sub>y</sub>(C) is smaller than between 2p<sub>x</sub>(O) and 2s(C).
10. The degenerate bonding  $\pi$  orbitals  $\psi_5$  and  $\psi_6$  will have lesser energies than the more stable constituent orbitals, i.e.  $\psi_{2+}$  and  $\psi_{3+}$ , respectively.
11. The degenerate antibonding  $\pi$  orbitals  $\psi_7$  and  $\psi_8$  will have more energies than the lesser stable constituent orbitals, i.e. 2p<sub>x</sub>(C) and 2p<sub>y</sub>(C), respectively.
12. The orbitals  $\psi_5$  and  $\psi_7$  will be less stable than  $\psi_4$  as side-way overlapping between 2p<sub>x</sub>(C) and 2p<sub>y</sub>(C) or 2p<sub>y</sub>(C) and 2p<sub>x</sub>(O) will be smaller than the lateral overlapping between 2p<sub>x</sub>(C) and 2p<sub>x</sub>(O). Similarly, the orbitals  $\psi_6$  and  $\psi_8$  will be more stable than the orbitals  $\psi_2$  and  $\psi_3$ .
13. The group orbitals  $\psi_{2-}$  and  $\psi_{3-}$  will be more or less nonbonding orbitals.

Keeping in mind the above factors, the relative orbital energies of carbon dioxide can be drawn, and is shown in Fig. 2.14.16. Since there are sixteen valence electrons (four from carbon and six from each oxygen), the electronic configuration of  $\text{CO}_2$  is

$$[2s(\text{O})]^{-2} [2s(\text{O})]^{-2} (\psi_1)^2 (\psi_4)^2 (\psi_5)^2 (\psi_6)^2 (\psi_2)^2 (\psi_3)^2$$

There will be two  $\sigma$  bonds (due to  $\psi_1^2$  and  $\psi_4^2$ ), two  $\pi$  bonds (due to  $\psi_5^2$  and  $\psi_6^2$ ) and two lone pairs of electrons (due to  $\psi_2^2$  and  $\psi_3^2$ ).



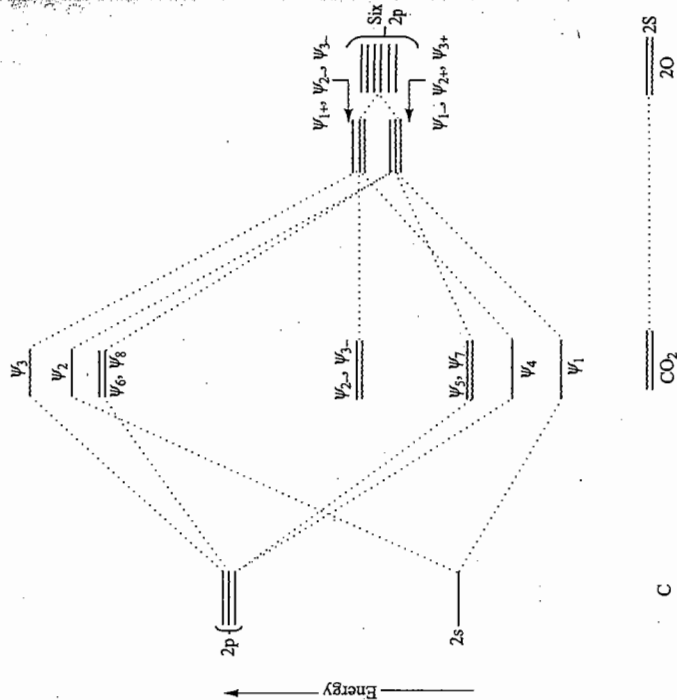


Fig. 2.14.16 Relative orbital energies for  $\text{CO}_2$

### Localized Molecular Orbitals of Carbon Dioxide

The localized bond of carbon dioxide is shown in Fig. 2.14.17. There are: (i) two  $\sigma$  bonds formed by the overlapping of  $\text{sp}_1(\text{O}_a)$  and of  $\text{sp}_2(\text{C})$  with  $\text{p}_x(\text{O}_a)$ ;  $\text{p}_y(\text{O}_b)$  or alternatively between  $\text{p}_x(\text{C})$  with  $\text{p}_x(\text{O}_a)$  and of  $\text{p}_y(\text{C})$  with  $\text{p}_y(\text{O}_b)$  and two lone pairs of electrons (one pair in  $\text{p}_y(\text{O}_a)$  and the other in  $\text{p}_x(\text{O}_b)$  or alternatively one pair in  $\text{p}_x(\text{O}_a)$  and the other in  $\text{p}_y(\text{O}_b)$ ). The localized bonds will be described by the following expressions:

$$\begin{aligned}\psi'_{1, \text{loc}} &= C'_1 \psi_{\text{sp}_1(\text{C})} - C'_2 \psi_{2p_z(\text{O}_b)} \\ &= C'_1 (\psi_{2s(\text{C})} + \psi_{2p_z(\text{C})}) - C'_2 \psi_{2p_z(\text{O}_b)}\end{aligned}\quad (2.14.21)$$

$$\begin{aligned}\psi'_{2, \text{loc}} &= C'_1 \psi_{\text{sp}_2(\text{C})} + C'_2 \psi_{2p_z(\text{O}_a)} \\ &= C'_1 (\psi_{2s(\text{C})} - \psi_{2p_z(\text{C})}) + C'_2 \psi_{2p_z(\text{O}_a)}\end{aligned}\quad (2.14.22)$$

$$\psi'_{3, \text{loc}} = C'_3 \psi_{2p_x(\text{C})} + C'_4 \psi_{2p_x(\text{O}_a)}\quad (2.14.23)$$

$$\psi'_{4, \text{loc}} = C'_3 \psi_{2p_y(\text{C})} + C'_4 \psi_{2p_y(\text{O}_b)}\quad (2.14.24)$$

$$\psi'_{5, \text{loc}} = \psi_{2p_y(\text{O}_a)}\quad (2.14.25)$$

$$\psi'_{6, \text{loc}} = \psi_{2p_x(\text{O}_b)}\quad (2.14.26)$$

Fig. 2.14.17 Valence-bond structures for  $\text{CO}_2$

### Conversion of Localized to Nonlocalized MOs

The localized molecular orbitals can be converted into nonlocalized molecular orbitals by the following combinations.

$$\begin{aligned}\psi_1 &= \psi'_{1, \text{loc}} + \psi'_{2, \text{loc}} \\ &= C'_1 \psi_{2s(\text{C})} + C'_2 (\psi_{2p_z(\text{O}_a)} - \psi_{2p_z(\text{O}_b)}) \\ \psi_4 &= \psi'_{1, \text{loc}} - \psi'_{2, \text{loc}} \\ &= C'_1 \psi_{2p_z(\text{C})} - C'_2 (\psi_{2p_z(\text{O}_a)} + \psi_{2p_z(\text{O}_b)}) \\ \psi_5 &= \psi'_{3, \text{loc}} + C'_4 \psi'_{6, \text{loc}} \\ &= C'_3 \psi_{2p_x(\text{C})} + C'_4 (\psi_{2p_x(\text{O}_a)} + \psi_{2p_x(\text{O}_b)}) \\ \psi_7 &= \psi'_{4, \text{loc}} + C'_4 \psi'_{5, \text{loc}} \\ &= C'_3 \psi_{2p_y(\text{C})} + C'_4 (\psi_{2p_y(\text{O}_a)} + \psi_{2p_y(\text{O}_b)})\end{aligned}$$

The functions  $\psi_1$ ,  $\psi_4$ ,  $\psi_5$  and  $\psi_7$  are, in fact, the same as described earlier by Eqs (2.14.13), (2.14.16), (2.14.17) and (2.14.19), respectively.

The schematic construction of correlation diagram may be carried out by following the steps given below.

1. Depict the relative energies of atomic orbitals of O and C atoms: Since oxygen is more electronegative than carbon, the 2s and 2p orbitals of oxygen are more stable than the corresponding orbitals of carbon.

### Correlation Diagram

2. Depict the sp hybridization of carbon orbitals: The energies of sp hybrid orbitals will be greater than that of 2s orbitals but smaller than that of 2p orbital.
3. Depict the formation of localized molecular orbitals: There will be (i) two degenerate  $\sigma$  bonding orbitals  $\psi'_{1, \text{loc}}$  and  $\psi'_{2, \text{loc}}$ ; (ii) two degenerate  $\sigma$  antibonding orbitals (the positive and negative combinations in Eqs 2.14.21 and 2.14.22, respectively), (iii) two degenerate  $\pi$  bonding orbitals  $\psi'_{3, \text{loc}}$  and  $\psi'_{4, \text{loc}}$ ; (iv) two degenerate  $\pi$  antibonding orbitals (the negative combinations in Eqs 2.14.23 and 2.14.24), and (v) two degenerate 2p nonbonding orbitals  $\psi'_{5, \text{loc}}$  and  $\psi'_{6, \text{loc}}$ .
4. The energies of two  $\sigma$  bonding orbitals will be smaller than those of  $\pi$  orbitals.
5. The energies of two  $\sigma$  antibonding orbitals will be larger than those of  $\pi$  antibonding orbitals.

Figure 2.14.18 exhibits the expected correlation diagram. Since  $\text{CO}_2$  has sixteen valence electrons, its configuration is

$$(\psi_{2s(\text{O})})^2 (\psi_{2s(\text{O})})^2 (\psi'_{1, \text{loc}})^2 (\psi'_{2, \text{loc}})^2 (\psi'_{3, \text{loc}})^2 (\psi'_{4, \text{loc}})^2 (\psi'_{5, \text{loc}})^2 (\psi'_{6, \text{loc}})^2$$

Figure 2.14.18 also exhibits the change in energies of localized molecular orbitals when they are converted into nonlocalized molecular orbitals.

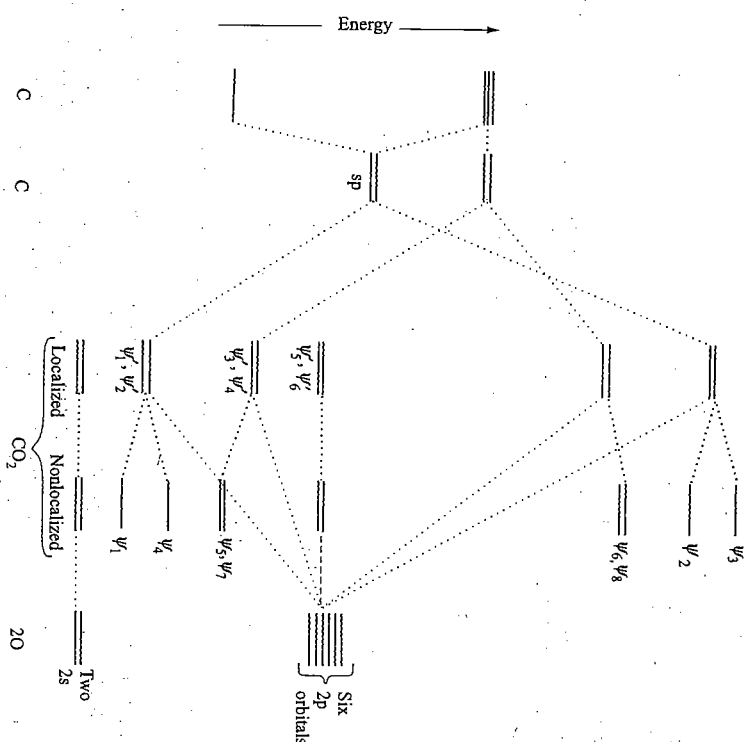


Fig. 2.14.18  
Correlation diagram of  
 $\text{CO}_2$ . The localized  
orbitals are simply  
written as  $\psi'_1, \psi'_2$ , etc.

### Problem 2.14.1

#### Solution

- (a) Construct the localized molecular orbitals of HCN molecule.
- (b) Transform these localized molecular orbitals into nonlocalized molecular orbitals.
- (c) Draw the contour diagrams of nonlocalized molecular orbital.
- (d) Draw the energy level diagram correlating the energies of localized and nonlocalized molecular orbitals. Assume  $2s(\text{N})$  orbital as the nonbonding orbital.

(a) The HCN molecule has a linear structure with a single  $\sigma$  bond between C and H and three bonds (one  $\sigma$  and two  $\pi$ ) between C and N. The carbon atom is in the sp-hybrid state. The two sp-hybrid orbitals of carbon are generated as follows.

$$\begin{aligned} \text{(i)} \quad \psi_{\text{sp}_1} &= \psi_{2s(\text{C})} + \psi_{2p_z(\text{C})} \\ \text{(ii)} \quad \psi_{\text{sp}_2} &= \psi_{2s(\text{C})} - \psi_{2p_z(\text{C})} \end{aligned}$$

The shapes of these orbitals are shown in Fig. 2.14.19.

From Fig. 2.14.19, it follows that the two localized  $\sigma$  bonds between N and C, and H and C can be generated as follows.

$$\begin{aligned} \text{(iii)} \quad \psi_{1, \text{loc}} &= C_1 \psi_{\text{sp}_1(\text{C})} - C_2 \psi_{2p_z(\text{N})} \\ \text{(iv)} \quad \psi_{2, \text{loc}} &= C_3 \psi_{\text{sp}_2(\text{C})} + C_4 \psi_{1s(\text{H})} \end{aligned}$$

The antibonding counterparts will be given by

$$\begin{aligned} \text{(v)} \quad \psi'_{1, \text{loc}} &= C'_1 \psi_{\text{sp}_1(\text{C})} + C'_2 \psi_{2p_z(\text{N})} \\ \text{(vi)} \quad \psi'_{2, \text{loc}} &= C'_3 \psi_{\text{sp}_2(\text{C})} - C'_4 \psi_{1s(\text{H})} \end{aligned}$$

The two  $\pi$  bonds between C and N will be represented by the following combinations.

$$\begin{aligned} \text{(vii)} \quad \psi_{3, \text{loc}} &= C_5 \psi_{2p_x(\text{C})} + C_6 \psi_{2p_x(\text{N})} \\ \text{(viii)} \quad \psi_{4, \text{loc}} &= C_7 \psi_{2p_y(\text{C})} + C_8 \psi_{2p_y(\text{N})} \end{aligned}$$

The orbitals  $\psi_{3, \text{loc}}$  and  $\psi_{4, \text{loc}}$  are degenerate with  $C_5 = C_7$  and  $C_6 = C_8$ . The antibonding counterparts will be given by

$$\begin{aligned} \text{(ix)} \quad \psi'_{3, \text{loc}} &= C'_5 \psi_{2p_x(\text{C})} - C'_6 \psi_{2p_x(\text{N})} \\ \text{(x)} \quad \psi'_{4, \text{loc}} &= C'_7 \psi_{2p_y(\text{C})} - C'_8 \psi_{2p_y(\text{N})} \end{aligned}$$

The two orbitals are also degenerate with  $C'_5 = C'_7$  and  $C'_6 = C'_8$ . There will be one nonbonding orbital comprising of  $2s(\text{N})$  orbital, i.e.

$$\text{(xi)} \quad \psi_{5, \text{loc}} = \psi_{2s(\text{N})}$$

(b) The two nonlocalized  $\sigma$  orbitals can be obtained by taking 'positive' and 'negative' combinations of  $\psi_{1, \text{loc}}$  and  $\psi_{2, \text{loc}}$ . Thus, we have

$$\psi_{1, \text{nl}} = \psi_{1, \text{loc}} + \psi_{2, \text{loc}}$$

$$= (C_1 + C_3) \psi_{2s(\text{C})} + (C_1 - C_3) \psi_{2p_z(\text{C})} - C_2 \psi_{2p_z(\text{N})} + C_4 \psi_{1s(\text{H})}$$

$$\psi_{2, \text{nl}} = \psi_{1, \text{loc}} - \psi_{2, \text{loc}}$$

$$= (C_1 - C_3) \psi_{2s(\text{C})} + (C_1 + C_3) \psi_{2p_z(\text{C})} - C_2 \psi_{2p_z(\text{N})} - C_4 \psi_{1s(\text{H})}$$

The two nonlocalized  $\sigma^*$  orbitals can be generated by taking 'negative' and 'positive' combinations of  $\psi'_{1, \text{loc}}$  and  $\psi'_{2, \text{loc}}$ . Thus, we have

$$\psi'_{1, \text{nl}} = \psi'_{1, \text{loc}} - \psi'_{2, \text{loc}}$$

$$= (C'_1 - C'_3) \psi_{2s(\text{C})} + (C'_1 + C'_3) \psi_{2p_z(\text{C})} + C'_2 \psi_{2p_z(\text{N})} + C'_4 \psi_{1s(\text{H})}$$

$$\psi'_{2, \text{nl}} = \psi'_{1, \text{loc}} + \psi'_{2, \text{loc}}$$

$$= (C'_1 + C'_3) \psi_{2s(\text{C})} + (C'_1 - C'_3) \psi_{2p_z(\text{C})} + C'_2 \psi_{2p_z(\text{N})} - C'_4 \psi_{1s(\text{H})}$$

If it is assumed that  $C_1 - C_3 \ll C_1 + C_3$  and  $C'_1 - C'_3 \ll C'_1 + C'_3$  the above four nonlocalized orbitals may be written as

$$\psi_{1, nl} = (C_1 + C_3)\psi_{2s(C)} - C_2\psi_{2p_z(N)} + C_4\psi_{1s(H)}$$

$$\psi_{2, nl} = (C_1 + C_3)\psi_{2p_z(C)} - C_2\psi_{2p_z(N)} - C_4\psi_{1s(H)}$$

$$\psi'_{1, nl} = (C'_1 + C'_3)\psi_{2p_z(C)} + C'_2\psi_{2p_z(N)} + C'_4\psi_{1s(H)}$$

$$\psi'_{2, nl} = (C'_1 + C'_3)\psi_{2s(C)} + C'_2\psi_{2p_z(N)} - C'_4\psi_{1s(H)}$$

The 'positive' and 'negative' combinations of  $\psi_{3, loc}$  and  $\psi_{4, loc}$  and  $\psi'_{3, loc}$  and  $\psi'_{4, loc}$  create the molecular orbitals which are of the same type as represented by  $\psi_{3, loc}$ ,  $\psi_{4, loc}$ ,  $\psi'_{3, loc}$  and  $\psi'_{4, loc}$  with the exception of change in the directions of molecular orbitals. Thus, the orbitals  $\psi_{3, loc}$ ,  $\psi_{4, loc}$ ,  $\psi'_{3, loc}$  and  $\psi'_{4, loc}$  may be treated as nonlocalized molecular orbitals. The nonbonding  $\psi_{5, loc}$  will also remain unchanged.

(c) The contour diagrams of nonlocalized molecular orbitals are shown in Fig. 2.14.20.

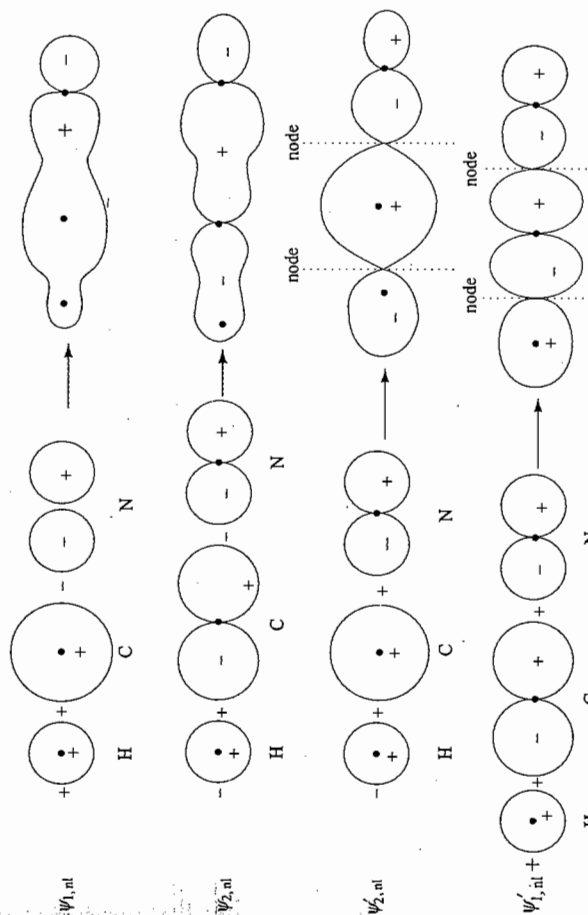


Fig. 2.14.20 The contour diagrams of nonlocalized molecular orbitals

(d) The relative order of energies of localized molecular orbitals follows from the following facts.

- (i) The energy of nonbonding orbital  $\psi_{5, loc}$  ( $\equiv \psi_{2s(N)}$ ) will have the smallest energy as N is the most electronegative atom in HCN molecule.
- (ii) The energy of  $\psi_{2, loc}$  will be smaller than that of  $\psi_{1, loc}$  as the overlapping between  $1s(H)$  and  $sp_1(C)$  will be larger than that between  $\psi_{2p_z(N)}$  and  $sp_2(C)$ .

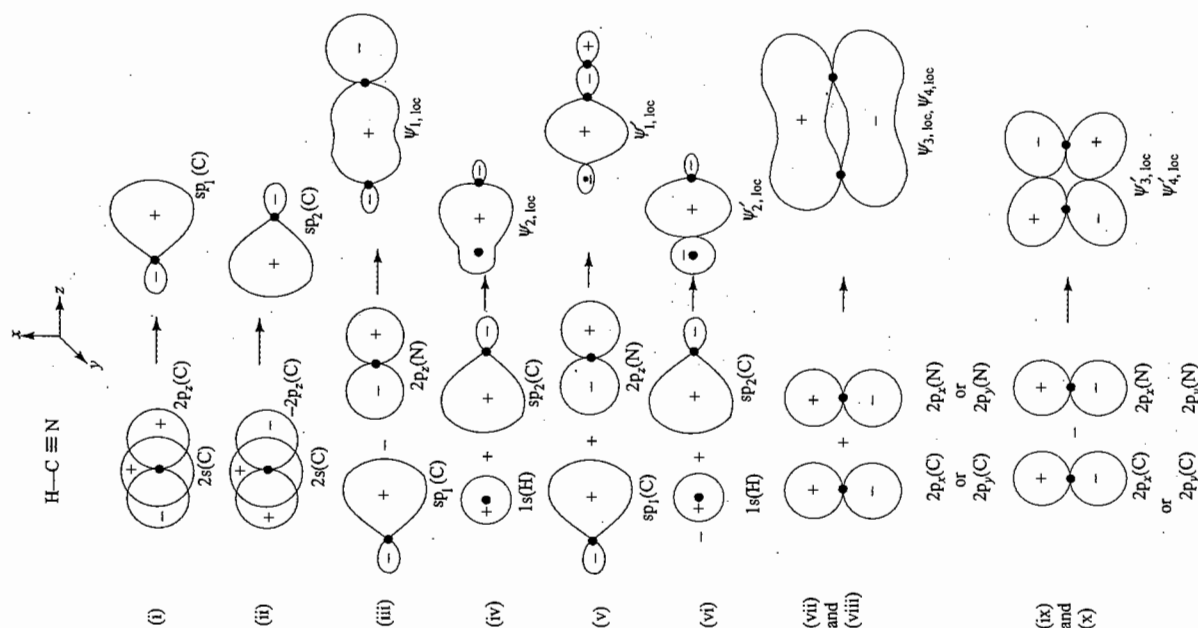


Fig. 2.14.19 The shapes of the two  $sp$ -hybrid orbitals of carbon and the formation of localized molecular orbitals (schematic)

- (iii) The energies of  $\psi_{3,loc}$  and  $\psi_{4,loc}$  which represent  $\pi$  orbitals, will be larger than  $\psi_{1,loc}$  as the side-way overlapping between  $2p(C)$  and  $2p(N)$  will be smaller than that between  $sp_1(C)$  and  $2p(N)$ . The functions  $\psi_{3,loc}$  and  $\psi_{4,loc}$  will be degenerate.
- (iv) The energies of antibonding  $\psi'_{3,loc}$  and  $\psi'_{4,loc}$  orbitals will be larger than that those of bonding  $\psi_{3,loc}$  and  $\psi_{4,loc}$  orbitals.
- (v) The energy of  $\psi'_{1,loc}$  will be larger than  $\psi'_{2,loc}$  since  $2p_z(N)$  orbital will lie above  $1s(H)$  orbital.

Keeping these facts in mind, the relative order of energies of orbitals is shown in Fig. 2.14.21. The relative order of energies of nonlocalized molecular orbitals can be derived from those of localized orbitals and is also shown in Fig. 2.14.21.

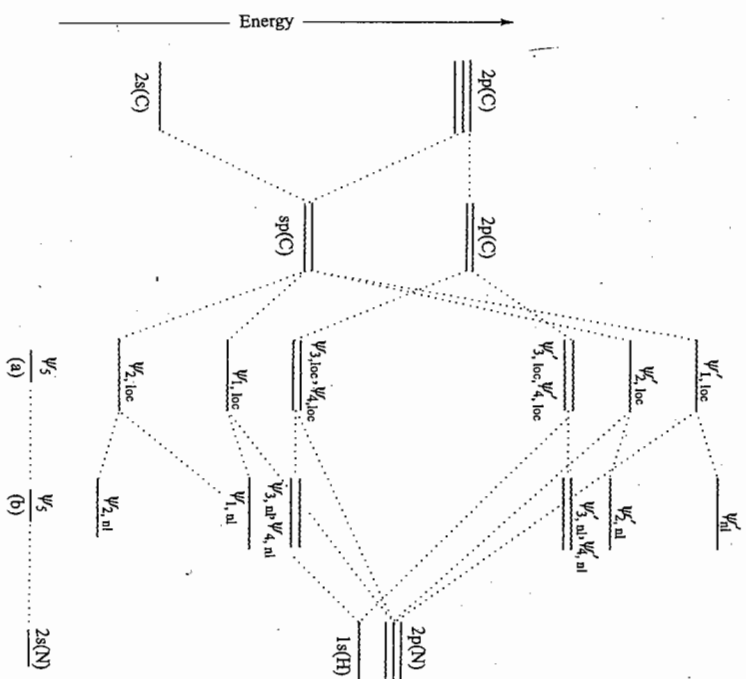


Fig. 2.14.21 The relative order of energies of (a) localized, and (b) nonlocalized orbitals in HCN molecule

## 2.15 CORRELATION OF THE ORBITALS FOR BENT AND LINEAR $AH_2$ MOLECULES

A.D. Walsh in 1953 correlated the molecular orbitals for bent and linear  $AH_2$  molecules and rationalized the following facts regarding the shapes of molecules in the ground states.

$AH_2$  molecules containing 4 valence electrons should be linear whereas those containing 5–8 valence electrons should be bent.

The types of molecular orbitals involved in bent and linear  $AH_2$  molecules are given in Table 2.15.1.

Table 2.15.1 Types of Orbitals Involved in Bent and Linear  $AH_2$  Molecules

Bent molecules	Linear molecules
1. Two bonding orbitals formed from:	1. Two bonding orbitals formed from:
(i) Group orbital $1s(H_a) + 1s(H_b)$ and $2p_z(A)$ when the bond angle is $90^\circ$ or $1s(H_a) + 1s(H_b)$ , $2s(A)$ and $2p_z(A)$ when the bond angle $> 90^\circ$ and $< 180^\circ$ , e.g. Eq. (2.14.7).	(i) Group orbital $1s(H_a) + 1s(H_b)$ and $2s(A)$ , e.g. Eq. (2.14.1).
(ii) Group orbital $1s(H_a) - 1s(H_b)$ and $2p_x(A)$ or $2p_y(A) + 2p_z(A)$ , e.g. Eq. (2.14.8).	(ii) Group orbital $1s(H_a) - 1s(H_b)$ and $2p_x(A)$ , e.g. Eq. (2.14.4).
2. Two nonbonding orbitals: one is $2s(A)$ orbital and the other is $2p_y(A)$ or $2p_x(A) - 2p_z(A)$ orbital.	2. Two nonbonding p orbitals centred on A

When the bond angle of bent  $AH_2$  molecule is gradually increased from  $90^\circ$  to  $180^\circ$  (linear structure), the following changes in energies of orbital occurs.

### 1. The bonding orbital

$$\psi_{1,b} = C'_1 (\psi_{1s(H_a)} + \psi_{1s(H_b)}) + C'_2 \psi_{2p_z(A)}$$

is changed to

$$\psi_{1,b} = C'_1 (\psi_{1s(H_a)} + \psi_{1s(H_b)}) + C'_2 \psi_{2p_z(A)} + C'_3 \psi_{2s(A)}$$

when bond angle  $> 90^\circ$  and  $< 180^\circ$ , and finally to

$$\psi_{1,lin} = C'_1 (\psi_{1s(H_a)} + \psi_{1s(H_b)}) + C'_2 \psi_{2s(A)}$$

when the bond angle is  $180^\circ$ . The subscripts b and lin stand for bent and linear structures, respectively. This means that the participation of  $2s$  orbital centred on A (which is nonbonding in the bent structure) in the molecular orbital increases as the bond angle is increased from  $90^\circ$  to  $180^\circ$ . As a consequence of this, the orbital energy decreases as the molecule is gradually changed from bent to the linear structure. In the latter,  $2p_z(A)$  orbital becomes nonbonding in place of  $2s(A)$  orbital in the bent structure.

### 2. The form of molecular orbital

$$\psi_{2,b \text{ or lin}} = C_1 (\psi_{1s(H_a)} - \psi_{1s(H_b)}) + C_2 \psi_{2p_z(A)}$$

remains unchanged in converting bent structure to the linear structure. The group orbital  $\psi_{1s(H_a)} - \psi_{1s(H_b)}$  of the end atoms of the molecule is antibonding and it is known that the molecular orbital formed from such group orbital is stable when the end atoms are as far apart as possible (i.e. in the linear molecule)<sup>†</sup>. Thus the energy of orbital  $\psi_2$  decreases as the molecule is gradually changed from bent to the linear structure.

<sup>†</sup> If the orbital is bonding between the end atoms, it is most stable if the end atoms are near to each other (i.e. in the bent structure).

3. One of the two nonbonding orbitals is  $p$  orbital in both the structures and hence its energy remains constant during the change of structure of the molecule. The second nonbonding orbitals in bent structure is  $2s(A)$  orbital whereas in the linear structure, it is  $2p(A)$  orbital. Since during the structural changes from bent to linear, the  $2p(A)$  orbital in the molecular orbital  $\psi_1$  is replaced by  $2s(A)$  orbital, it is obvious that the nonbonding  $2s(A)$  orbital in the bent structure becomes  $2p(A)$  orbital in the linear structure. Thus, the energy of this nonbonding orbital increases steeply until it becomes one of the degenerate  $p$  orbitals at  $180^\circ$ .

Figure 2.15.1 depicts the correlation diagram between the four orbitals described above for bent and linear  $AH_2$  molecules. From Fig. 2.15.1, it may be concluded that the  $AH_2$  molecules having 4-valence electrons will have the lowest energy if its structure is linear, i.e. the stable structure for  $AH_2$  molecules having 4-valence electrons is the linear structure. The molecules having 5, 6, 7 or 8 valence electrons are not expected to have linear structure as it is possible to write down electronic configuration corresponding to the bent structure which has minimum energy, i.e. the molecules having 5, 6, 7 or 8 valence electrons are expected to be nonlinear. As examples, the  $BeH_2$  and  $HgH_2$  molecules are expected to be linear in their ground states whereas the  $CH_2$ ,  $OH_2$ ,  $SH_2$  molecules are expected to be nonlinear in their ground states. The first excited state of  $BeH_2$  or  $HgH_2$  is expected to be nonlinear.

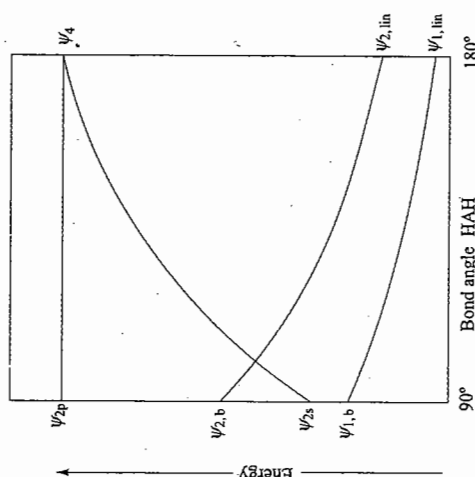


Fig. 2.15.1 Qualitative variation of molecular orbital energies with bond angle HAH

The actual electronic configuration of bent molecules having bond angle close to  $180^\circ$  cannot be predicted with certainty as the existence of electron repulsion may offset the small energy difference between the two nonbonding orbitals. For example, if the bond angle of  $CH_2$  molecule is close to  $180^\circ$ , the electronic configuration

$$(\psi_{1,lin})^2(\psi_{2,lin})^2(\psi_{3,lin})^1(\psi_{4,lin})^1 \quad (2.15.1)$$

has lower energy than

$$(\psi_{1,b})^2(\psi_{2,b})^2(\psi_{3,b})^2(\psi_{4,b})^2 \quad (2.15.2)$$

If, on the other hand, the apex angle is considerably less than  $180^\circ$ , the ground state will have the configuration as given by Eq. (2.15.2).

A similar study on  $AB_2$  and  $BAC$  molecules by Walsh rationalized the following facts regarding their shapes.

*The molecules with not more than 16 valence electrons are linear in their ground states; the molecules with 17, 18, 19 or 20 valence electrons are bent in their ground states, the apex angle decreases markedly from 16- to 17- and from 17- to 18- electron molecules and less markedly from 18- to 19- and 19- to 20- electron molecules; the molecules with 22 electrons are linear or very linear in their ground states.*

For molecules  $HAB$ , Walsh obtained the following facts:

*The molecules having 10 and 16 valence electrons are linear whereas those having 11-14 electrons are bent.*

Examples of linear  $HAB$ ,  $AB_2$  and  $BAC$  molecules are given in Table 2.15.2.

Table 2.15.2 Examples of Linear and Nonlinear Molecules

Valence electrons	Structure	Examples
10	linear	HCN
11	nonlinear	HCO
12	nonlinear	HNO
13	nonlinear	HO <sub>2</sub>
14	nonlinear	HOCl
16	linear	FHF <sup>-</sup>
12	linear	C <sub>3</sub>
13	linear	CCN
14	linear	NCN
15	linear	NCO
15	linear	CO <sub>2</sub> <sup>+</sup>
16	linear	NO <sub>2</sub> <sup>+</sup> , CO <sub>2</sub> , COS, CS <sub>2</sub> , N <sub>2</sub> O, ClCN, HgCl <sub>2</sub> , NCO <sup>-</sup> , N <sub>3</sub> <sup>-</sup> , AgCl <sub>2</sub> <sup>+</sup> and AuCl <sub>2</sub> <sup>+</sup>
17	nonlinear	NO <sub>2</sub>
18	nonlinear	NOCl, NOBr, NO <sub>2</sub> <sup>-</sup> , O <sub>3</sub>
19	nonlinear	ClO <sub>2</sub> , NF <sub>2</sub>
20	nonlinear	F <sub>2</sub> O, Cl <sub>2</sub> O, Cl <sub>2</sub> S
22	linear	BrBr <sup>+</sup> , CHCl <sup>+</sup> , I <sub>3</sub> , KrF <sub>2</sub> <sup>+</sup> , XeF <sub>2</sub> <sup>+</sup>

## 2.16 CONJUGATED ORGANIC MOLECULES

A conjugated organic molecule involves an alternate arrangement of single and double bonds between carbon atoms. The bonding in these molecules can be

explained on the basis of  $sp^2$  hybrid orbitals of carbon atoms. The single bond constitutes a  $\sigma$  bond formed by the overlapping of the two  $sp^2$  hybrid orbitals of neighbouring carbon atoms. The double bond contains one  $\sigma$  and one  $\pi$  bond. The former is formed again by overlapping of two  $sp^2$  hybrid carbon orbitals and the latter is formed by the side-way overlapping of the  $p_z$  orbitals.<sup>†</sup>

The entire molecule can be treated semiempirically by the molecular orbital method.<sup>††</sup> But because of the fact that various  $\sigma$  bonds lie in the  $xy$ -plane and  $p_z$  orbitals perpendicular to this plane, we may expect that the latter's do not take part in the formation of  $\sigma$  bonds. Thus, various  $p_z$  orbitals and the other orbitals ( $s$ ,  $p_x$  and  $p_y$ ) may be treated separately under the LCAO-MO framework.<sup>‡</sup>

In this section, we focus our attention on the  $\pi$ -electrons of conjugated organic molecules. In the molecular orbital theory, these  $\pi$ -electrons are considered to be distributed over the  $\pi$ -molecular orbitals extended over the entire molecule. These molecular orbitals may be constructed by the linear combination of carbon  $2p_z$  orbitals, i.e.

$$\psi_\pi = \sum_{i=1}^n C_i \psi_{2p_z(i)} \quad (2.16.1)$$

where  $n$  represents the number of  $p_z$  orbitals in the molecule. The coefficients in Eq. (2.16.1) as usual can be determined by the variation method. The latter will give us  $n$  simultaneous linear secular equations:

$$C_1(H_{11} - ES_{11}) + C_2(H_{12} - ES_{12}) + \dots + C_n(H_{1n} - ES_{1n}) = 0$$

$$C_1(H_{21} - ES_{21}) + C_2(H_{22} - ES_{22}) + \dots + C_n(H_{2n} - ES_{2n}) = 0$$

⋮

$$C_1(H_{n1} - ES_{n1}) + C_2(H_{n2} - ES_{n2}) + \dots + C_n(H_{nn} - ES_{nn}) = 0 \quad (2.16.2)$$

$$\text{where } H_{ii} = \int \psi_{2p_z(i)} |H_{op}| \psi_{2p_z(i)} d\tau \quad (2.16.3a)$$

$$H_{ij} = \int \psi_{2p_z(i)} |H_{op}| \psi_{2p_z(j)} d\tau \quad (2.16.3b)$$

$$S_{ii} = \int \psi_{2p_z(i)} \psi_{2p_z(i)} d\tau \quad (2.16.3c)$$

$$S_{ij} = \int \psi_{2p_z(i)} \psi_{2p_z(j)} d\tau \quad (2.16.3d)$$

<sup>†</sup> The entire skeleton of a conjugated molecule lies in a plane (taken to be  $xy$ -plane). The  $z$ -axis lies perpendicular to the plane of molecule.

<sup>††</sup> One of the methods is the extended Hückel molecular orbital method where LCAO-MO framework is applied to all valence orbitals of atoms in a molecule.

<sup>‡</sup> This separation basically is due to the fact that the overlap integrals between  $s$  and  $p_x$ ,  $p_y$  and  $p_z$  orbitals will be zero.

### Hückel Approximation

For the nontrivial roots, we set  $n \times n$  secular determinant equal to zero, i.e.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2n} - ES_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots & H_{nn} - ES_{nn} \end{vmatrix} = 0 \quad (2.16.4)$$

In principle, the above determinant can be solved for the various energy values. These when substituted one by one in secular equations (Eqs 2.16.2) along with the normalization condition of the molecular orbital give the  $n$  coefficients of the corresponding molecular orbitals.

In general, the evaluation of various integrals in Eq. (2.16.4) cannot be carried out in a reasonably exact way. In order to make the calculations simple enough to be useful to the average chemist, Hückel introduced the drastic approximations regarding the values of integrals in Eq. (2.16.4). In spite of the drastic approximations, the Hückel method has been found to be very useful in understanding many important features of  $\pi$  bondings. The approximations introduced by Hückel are:

- All overlap integrals  $S_{ij}$  are assumed to be equal to zero. Since the atomic orbitals are normalized,  $S_{ii} = 1$ .
- $H_{ii}$  is assumed to be the same for all the carbon atoms involved. It is usually represented by the symbol  $\alpha$  and is called the *Coulomb integral*. It is generally treated as an unknown parameter.
- $H_{ij}$  is assumed to have the constant value  $\beta$  if atoms  $i$  and  $j$  are bonded directly. All other  $H_{ij}$ 's are set equal to zero. The term  $\beta$  is called the *resonance integral* and is again regarded as an adjustable parameter.

To illustrate the above approximations, we describe below the Hückel molecular orbital calculations on ethylene, butadiene and benzene molecules.

#### ETHYLENE MOLECULE

Figure 2.16.1 illustrates the ethylene molecule.

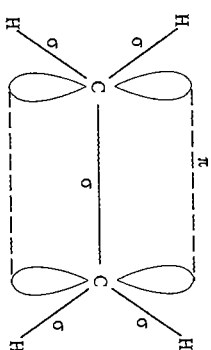


Fig. 2.16.1 An ethylene molecule

The secular determinant will take the form

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \quad (2.16.5)$$

Dividing each element of the above determinant by  $\beta$  and then setting  $(\alpha - E)/\beta = x$ , we get

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

which on expanding gives

$$x^2 - 1 = 0$$

The two roots of the above equation are

$$x = -1 \text{ and } +1$$

$$\text{Thus } \frac{\alpha - E}{\beta} = -1 \quad \text{and} \quad \frac{\alpha - E}{\beta} = 1$$

which gives  $E_+ = \alpha + \beta$

$$E_- = \alpha - \beta \quad (2.16.6b)$$

Substituting these energies in the secular equations, we get

$$\psi_+ = C(\psi_{2p_z(1)} + \psi_{2p_z(2)}); \quad E_+ = \alpha + \beta \quad (2.16.7a)$$

$$\psi_- = C(\psi_{2p_z(1)} - \psi_{2p_z(2)}); \quad E_- = \alpha - \beta \quad (2.16.7b)$$

The value of  $C$  as determined by normalizing the molecular orbital  $\psi_+$  or  $\psi_-$  is

$$C = \frac{1}{\sqrt{2}} \quad (2.16.8)$$

Thus for ethylene, we have two  $\pi$ -molecular orbitals. Since both  $\alpha$  and  $\beta$  have negative values, we may conclude that

$$E_+ < E_-$$

The function  $\psi_+$  is the bonding orbital and  $\psi_-$  is the antibonding orbital. The ground state  $\pi$ -electronic configuration is  $\psi_+(1)\psi_+(2)$ . The ground state electronic energy is

$$2(\alpha + \beta) \quad (2.16.9)$$

Since  $\beta$  is a negative quantity, the above energy is less than the sum of energies of electrons ( $= 2\alpha$ ) in the two  $p_z$  orbitals.

### BUTADIENE MOLECULE

Figure 2.16.2 illustrates the butadiene molecule.

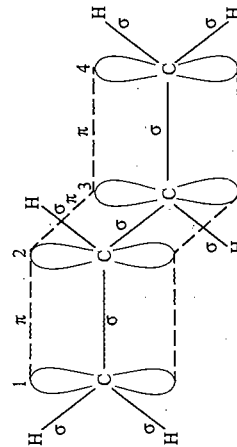


Fig. 2.16.2 A  
butadiene molecule

The scalar determinant will take the form

$$\begin{vmatrix} \alpha - \beta & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad (2.16.10)$$

Dividing each element of the above determinant by  $\beta$  and then setting  $(\alpha - E)/\beta = x$ , we get

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

which on expanding gives

$$x^4 - 3x^2 + 1 = 0$$

The four roots of the above equation are

$$-1.618, -0.618, +0.618 \text{ and } +1.618$$

The corresponding four values of energy are

$$E_1 = \alpha + 1.618 \beta \quad (2.16.11a)$$

$$E_2 = \alpha + 0.618 \beta \quad (2.16.11b)$$

$$E_3 = \alpha - 0.618 \beta \quad (2.16.11c)$$

$$E_4 = \alpha - 1.618 \beta \quad (2.16.11d)$$

Since  $\beta$  is negative, it follows that

$$E_1 < E_2 < E_3 < E_4$$

The coefficients of molecular orbitals corresponding to the above energies can be obtained by substituting the above energies one by one in the secular equations, which in the present case are

$$\begin{cases} C_1(\alpha - E) + C_2\beta = 0 \\ C_1\beta + C_2(\alpha - E) + C_3\beta = 0 \\ C_2\beta + C_3(\alpha - E) + C_4\beta = 0 \\ C_3\beta + C_4(\alpha - E) = 0 \end{cases} \quad (2.16.12)$$

For example, if we substitute  $E_1$  from Eq. (2.16.11a) in Eqs (2.16.12), we get

$$\begin{cases} -1.618 C_1\beta + C_2\beta = 0 \\ C_1\beta - 1.618 C_2\beta + C_3\beta = 0 \\ C_2\beta - 1.618 C_3\beta + C_4\beta = 0 \\ C_3\beta - 1.618 C_4\beta = 0 \end{cases} \quad (2.16.13)$$

Dividing by  $\beta$  and applying the normalizing condition

$$C_1^2 + C_2^2 + C_3^2 + C_4^2 = 1$$

we get  $C_1 = C_4 = 0.372$

and  $C_2 = C_3 = 0.602$

Thus, the molecular orbital having energy  $E_1$  is

$$\psi_1 = 0.372\psi_{2p_z(1)} + 0.602\psi_{2p_z(2)} + 0.602\psi_{2p_z(3)} + 0.372\psi_{2p_z(4)} \quad (2.16.15a)$$

The molecular orbitals having the remaining energies can be determined in the same way; they are

$$\psi_2 = 0.602\psi_{2p_z(1)} + 0.372\psi_{2p_z(2)} - 0.372\psi_{2p_z(3)} - 0.602\psi_{2p_z(4)} \quad (2.16.15b)$$

$$\psi_3 = 0.602\psi_{2p_z(1)} - 0.372\psi_{2p_z(2)} - 0.372\psi_{2p_z(3)} + 0.602\psi_{2p_z(4)} \quad (2.16.15c)$$

$$\psi_4 = 0.372\psi_{2p_z(1)} - 0.602\psi_{2p_z(2)} + 0.602\psi_{2p_z(3)} - 0.372\psi_{2p_z(4)} \quad (2.16.15d)$$

These molecular orbitals are represented schematically in Fig. 2.16.3.

The number of nodes present in the wave functions  $\psi_1$ ,  $\psi_2$ ,  $\psi_3$  and  $\psi_4$  are also shown in Fig. 2.16.3. The wave function  $\psi_1$  does not contain any node and is thus a strongly bonding orbital. The function  $\psi_2$  has a node between second and third carbon atoms. It has a partial bonding character as it accumulates charges between atoms 1 and 2, and 3 and 4 (isolated double bonds). The functions  $\psi_3$  and  $\psi_4$  are antibonding since their energies are greater than that of an isolated  $p_z$  orbital.

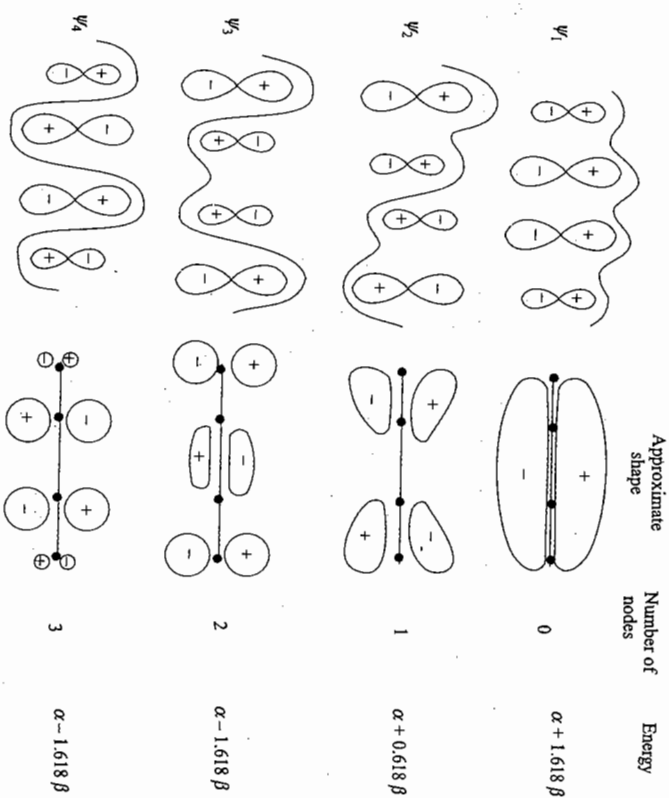


Fig. 2.16.3  
Schematic graph of  
four  $\pi$ -molecular  
orbitals of butadiene

### Delocalization Energy

The butadiene molecule contains four  $\pi$ -electrons and thus its ground state electronic configuration is

$$(\psi_1)^2(\psi_2)^2$$

with the ground-state energy

$$E = 2E_1 + 2E_2$$

$$= 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$$

$$= 4\alpha + 4.472\beta$$

(2.16.16)

If we had considered a butadiene molecule to consist of two isolated double bonds, the total energy of the system would have been  $4\alpha + 4\beta$ . The difference between the above energy and the energy of butadiene (Eq. 2.16.16) is  $0.472\beta$ . This difference of energy is called the delocalization energy and has a negative value as  $\beta$  is a negative quantity. Thus, delocalization of  $\pi$ -electrons over the entire molecule has made it more stable by an amount  $0.472\beta$ .

### BENZENE MOLECULE

Figure 2.16.4 displays the benzene molecule.

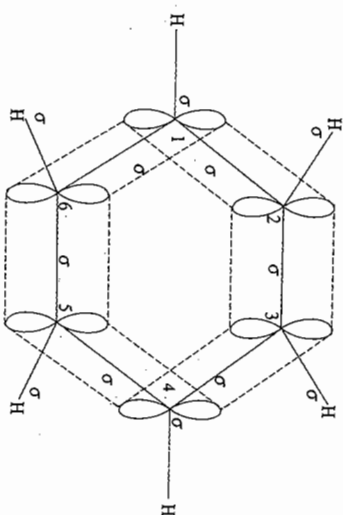


Fig. 2.16.4 Display  
of benzene molecule

The secular determinant in the present case is

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad (2.16.17)$$



Dividing each element by  $\beta$  and replacing  $(\alpha - E)/\beta$  by  $x$ , we get

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \quad (2.16.18)$$

The expansion of determinants such as this by an elementary method is a tedious process.<sup>†</sup> We report the final expression for the above determinant which is

$$x^6 - 6x^4 + 9x^2 - 4 = (x^2 - 4)(x^2 - 1)^2 = 0$$

Thus, its roots are

$$\pm 2, \pm 1 \text{ and } \pm 1$$

Hence, the six energy expressions are

$$E_1 = \alpha + 2\beta$$

$$\begin{matrix} E_2 \\ E_3 \end{matrix} = \alpha + \beta$$

$$\begin{matrix} E_4 \\ E_5 \end{matrix} = \alpha - \beta$$

$$E_6 = \alpha - 2\beta$$

The first three energy values are lower than  $\alpha$ , and the corresponding molecular orbitals are bonding molecular orbitals. The other three molecular orbitals are antibonding molecular orbitals. The energies  $E_2$  and  $E_3$ , and  $E_4$  and  $E_5$  constitute the degenerate levels.

The coefficients in the wave function can be determined as usual and are given below.

$$\psi_1 = \frac{1}{\sqrt{6}} (\psi_{2p_z(1)} + \psi_{2p_z(2)} + \psi_{2p_z(3)} + \psi_{2p_z(4)} + \psi_{2p_z(5)} + \psi_{2p_z(6)})$$

$$\psi_2 = \frac{1}{2} (\psi_{2p_z(2)} + \psi_{2p_z(3)} - \psi_{2p_z(5)} - \psi_{2p_z(6)})$$

$$\psi_3 = \frac{1}{2\sqrt{3}} (2\psi_{2p_z(1)} + \psi_{2p_z(2)} - \psi_{2p_z(3)} - \psi_{2p_z(4)} - \psi_{2p_z(5)} + \psi_{2p_z(6)})$$

$$\psi_4 = \frac{1}{2} (\psi_{2p_z(2)} - \psi_{2p_z(3)} + \psi_{2p_z(5)} - \psi_{2p_z(6)})$$

<sup>†</sup> The roots can be determined by diagonalizing the matrix with the help of electronic computer. The diagonalization process not only determines the roots but also the coefficients of the corresponding molecular orbitals. Thus, the solution of a tedious and lengthy secular determinant can be done conveniently with the help of computers.

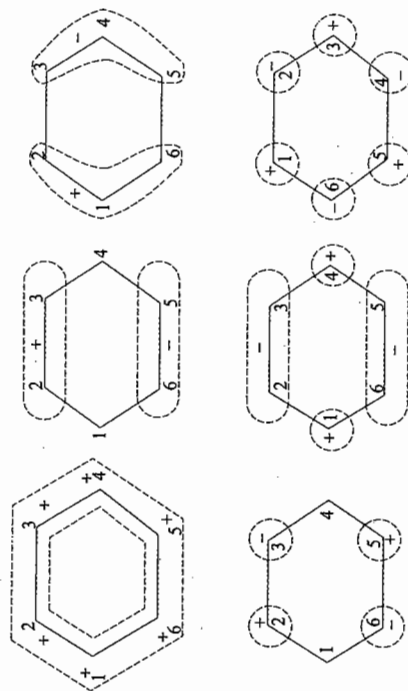


Fig. 2.16.5  
Schematic  
representation of 6  
 $\pi$ -orbitals of benzene  
(top view)

There are six  $\pi$ -electrons in benzene, hence its ground-state electronic configuration is

$$(\psi_1)^2(\psi_2)^2(\psi_3)^2$$

with the ground-state energy equal to

$$E = 2E_1 + 2E_2 + 2E_3 = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta \quad (2.16.19)$$

The delocalization energy is

$$(6\alpha + 8\beta) - (6\alpha + 6\beta) = 2\beta$$

### SOME USEFUL QUANTITIES

Some useful quantities pertaining to conjugated molecules are now described.

In general, we may write any molecular orbital as

$$\psi_j = \sum_{r=1}^n C_{jr} \psi_{2p_{z(r)}}$$

where the subscript  $j$  refers to the  $j$ th molecular orbital and the subscript  $r$  refers to the  $r$ th atom of the molecule. The quantity  $C_{jr}^2$  give the electron density on the  $r$ th atom due to the  $j$ th molecular orbital. The total  $\pi$ -electron density on atom  $r$  may be calculated from

$$q_r = \sum_{j, \text{occ}} n_j C_{jr}^2$$

where the summation is carried over the occupied molecular orbitals and  $n_j$  represents the number of electrons occupying the  $j$ th molecular orbital.

The sum of all the  $q_s$  equals the total number of electrons in the system.

**Examples:** For butadiene, we have

$$q_1 = 2C_{11}^2 + 2C_{21}^2 = 2(0.372)^2 + 2(0.602)^2 = 2(0.140) + 2(0.360) = 1.000$$

$$q_2 = 2C_{12}^2 + 2C_{22}^2 = 2(0.602)^2 + 2(0.372)^2 = 2(0.360) + 2(0.140) = 1.000$$

Similarly,  $q_3 = q_4 = 1.000$

In butadiene cation we have

$$q_1 = 2C_{11}^2 + C_{21}^2 = 2(0.372)^2 + (0.602)^2 = 0.640$$

$$q_2 = 2C_{12}^2 + C_{22}^2 = 2(0.602)^2 + (0.372)^2 = 0.860$$

$$q_3 = q_2$$

$$q_4 = q_1$$

The bond order between atoms  $r$  and  $s$  is defined as

$$P_{rs} = \sum_{j, \text{occ}} n_j C_{jr} C_{js}$$

The value of  $P_{rs}$  reflects the bonding power of the bond and is related to its bond length. One of the relations in use is

$$R_{rs}/\text{pm} = 151.7 - 18.0 P_{rs}$$

**Examples:** For butadiene, we have

$$P_{12} = 2C_{11}C_{12} + 2C_{21}C_{22} = 2(0.372)(0.602) + 2(0.602)(0.372) = 0.894$$

$$P_{23} = 2C_{12}C_{13} + 2C_{22}C_{23} = 2(0.602)(0.602) + 2(0.372)(-0.0372) = 0.447$$

Thus, the bond  $C_1-C_2$  has more double bond character than  $C_2-C_3$  bond. Consequently, the bond length  $C_1-C_2$  is smaller than that of  $C_2-C_3$ . In benzene, we find that

$$P_{12} = P_{23} = P_{34} = P_{45} = P_{56} = P_{61} = 0.667$$

that is, all the six bonds are identical in nature.

The free valence index of atom  $r$  is defined as

$$F_r = \sqrt{3} - N_r$$

where  $N_r$  is the sum of the bond order values for all bonds joining atom  $r$ . This index has been used as a measure of ease of attack at atom  $r$  by free radicals.

**Examples:** For butadiene, we have

$$F_1 = \sqrt{3} - P_{12} = 1.732 - 0.894 = 0.838$$

$$F_2 = \sqrt{3} - P_{12} - P_{23} = 1.732 - 0.894 - 0.447 = 0.391$$

thus, the terminal atoms are more reactive than the central atoms.

### Longest Wave Length of $\pi \rightarrow \pi^*$ Transition

### General Expressions of Energy

The electron on excitation from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) absorbs radiation which may be correlated with the longest wavelength of  $\pi \rightarrow \pi^*$  transition. Thus, for ethylene and butadiene we have

$$\Delta E_{\text{eth}} = (\alpha - \beta) - (\alpha + \beta) = -2\beta$$

$$\Delta E_{\text{buta}} = (\alpha - 0.618\beta) - (\alpha + 0.618\beta) = -1.236\beta$$

Thus, going from ethylene to butadiene, one observes bathochromic shift. In general, conjugation leads to the red (bathochromic) shift. The above expressions provide us one of the examples to estimate the value of  $\beta$ .<sup>†</sup>

The general expression of the Hückel molecular orbital energy levels is available for linear and cyclic polyenes. These may be used to derive the energies of various molecular orbitals for a molecule and to compute  $\pi \rightarrow \pi^*$  transition. These are:

**Linear polyenes**  $E_j = \alpha + 2\beta \cos \left( \frac{j\pi}{n+1} \right)$

where  $j = 1, 2, \dots$ , and  $n$  is the number of atoms in the molecule.

**Cyclic polyenes**  $E_j = \alpha + 2\beta \cos \left( \frac{2j\pi}{n} \right)$

where  $j = 0, \pm 1, \pm 2, \dots$ , and  $n$  is the number of atoms in the molecule.

For an atom different from carbon, we will have different values of  $\alpha$  and  $\beta$ . In order to introduce these heteroatom values with the least possible disturbance of the secular determinant they are usually represented by the equation

$$\alpha_X = \alpha_C + h_X \beta_{CC}$$

$$\beta_{CX} = k_{CX} \beta_{CC}$$

where  $h_X$  and  $k_{CX}$  are constants, and are dependent on the heteroatoms.

(a) Using the Hückel approximations, show that for the allyl radical  $\left( \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH} \\ | \\ \text{CH}_2 \end{smallmatrix} \right)$ , the wave functions and the corresponding energies are given by

$$\psi_1 = \frac{1}{2} \psi_{2p_z(1)} + \frac{1}{\sqrt{2}} \psi_{2p_z(2)} + \frac{1}{2} \psi_{2p_z(3)}; \quad E_1 = \alpha + \sqrt{2}\beta$$

$$\psi_2 = \frac{1}{\sqrt{2}} \psi_{2p_z(1)} - \frac{1}{\sqrt{2}} \psi_{2p_z(3)}; \quad E_2 = \alpha$$

$$\psi_3 = \frac{1}{2} \psi_{2p_z(1)} - \frac{1}{\sqrt{2}} \psi_{2p_z(2)} + \frac{1}{2} \psi_{2p_z(3)}; \quad E_3 = \alpha - \sqrt{2}\beta$$

(b) Calculate the electron densities and bond orders for (i) allyl radical, (ii) allyl cation, and (iii) allyl anion.

<sup>†</sup> The other methods involve the data on heat of hydrogenation on resonance energies.

### Free Valence Index

## Solution

(a) The secular determinant for allyl radical is given by

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0$$

Dividing each element of the above determinant by  $\beta$  and then setting  $(\alpha - E)/\beta = x$ , we get

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

which on expanding gives  $x^3 - 2x = 0$

The three roots of the above equation are  $-\sqrt{2}$ ,  $0$ ,  $\sqrt{2}$

The corresponding three values of energies are

$$E_1 = \alpha + \sqrt{2}\beta$$

$$E_2 = \alpha$$

$$E_3 = \alpha - \sqrt{2}\beta$$

The secular equations are

$$C_1x + C_2 = 0$$

$$C_1 + C_2x + C_3 = 0$$

$$C_2 + C_3x = 0$$

For  $x = -\sqrt{2}$ , we will have

$$-\sqrt{2}C_1 + C_2 = 0 \quad (1)$$

$$C_1 - \sqrt{2}C_2 + C_3 = 0 \quad (2)$$

$$C_2 - \sqrt{2}C_3 = 0 \quad (3)$$

Equations (1) and (2) suggest that

$$C_1 = \frac{C_2}{\sqrt{2}} \quad \text{and} \quad C_3 = \frac{C_2}{\sqrt{2}}$$

Using the normalization criterion

$$C_1^2 + C_2^2 + C_3^2 = 1$$

$$\left(\frac{C_2}{\sqrt{2}}\right)^2 + C_2^2 + \left(\frac{C_2}{\sqrt{2}}\right)^2 = 1$$

we get

$$C_2 = \pm \frac{1}{\sqrt{2}}$$

or

Thus, the first wave function is given by

$$\psi_1 = \frac{1}{2}\psi_{2p_z(1)} + \frac{1}{\sqrt{2}}\psi_{2p_z(2)} + \frac{1}{2}\psi_{2p_z(3)} \quad (\text{bonding})$$

Working out similarly with  $x = 0$  and  $x = \sqrt{2}$ , we get

$$\psi_2 = \frac{1}{\sqrt{2}}\psi_{2p_z(1)} - \frac{1}{\sqrt{2}}\psi_{2p_z(3)}; \quad (\text{nonbonding})$$

$$\psi_3 = \frac{1}{2}\psi_{2p_z(1)} - \frac{1}{\sqrt{2}}\psi_{2p_z(2)} + \frac{1}{2}\psi_{2p_z(3)}; \quad (\text{antibonding})$$

## (b) Allyl radical

$$q_1 = 2C_{11}^2 + C_{21}^2 = 2\left(\frac{1}{2}\right)^2 + \left(\frac{1}{\sqrt{2}}\right)^2 = 1$$

$$q_2 = 2C_{12}^2 + C_{22}^2 = 2\left(\frac{1}{\sqrt{2}}\right)^2 + 0 = 1$$

$$q_3 = 2C_{13}^2 + C_{23}^2 = 2\left(\frac{1}{2}\right)^2 + \left(\frac{-1}{\sqrt{2}}\right)^2 = 1$$

$$p_{12} = 2C_{11}C_{12} + C_{21}C_{22} = 2\left(\frac{1}{2}\right)\left(\frac{1}{\sqrt{2}}\right) + 0 = \frac{1}{\sqrt{2}}$$

$$p_{23} = 2C_{12}C_{13} + C_{22}C_{23} = 2\left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right) + 0 = \frac{1}{\sqrt{2}}$$

Note: First and second subscripts of the coefficients  $C$ s represent molecular orbital and atomic orbital, respectively.

## Allyl cation

$$q_1 = 2C_{11}^2 = 2\left(\frac{1}{2}\right)^2 = \frac{1}{2}$$

$$q_2 = 2C_{12}^2 = \left(\frac{1}{\sqrt{2}}\right)^2 = \frac{1}{2}$$

$$q_3 = 2C_{13}^2 = 2\left(\frac{1}{2}\right)^2 = \frac{1}{2}$$

$$p_{12} = 2C_{11}C_{12} = 2\left(\frac{1}{2}\right)\left(\frac{1}{\sqrt{2}}\right) = \frac{1}{\sqrt{2}}$$

$$p_{23} = 2C_{12}C_{13} = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right) = \frac{1}{\sqrt{2}}$$

## Allyl anion

$$q_1 = 2C_{11}^2 + 2C_{21}^2 = 2\left(\frac{1}{2}\right)^2 + 2\left(\frac{1}{\sqrt{2}}\right)^2 = 1.5$$

$$q_2 = 2C_{12}^2 + 2C_{22}^2 = 2\left(\frac{1}{\sqrt{2}}\right)^2 + 0 = 1$$

$$q_3 = 2C_{13}^2 + 2C_{23}^2 = 2\left(\frac{1}{2}\right)^2 + 2\left(-\frac{1}{\sqrt{2}}\right)^2 = 1.5$$

$$p_{12} = 2C_{11}C_{12} + 2C_{21}C_{22} = 2\left(\frac{1}{2}\right)\left(\frac{1}{\sqrt{2}}\right) + 0 = \frac{1}{\sqrt{2}}$$

$$p_{23} = 2C_{12}C_{13} + 2C_{22}C_{23} = 2\left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right) + 0 = \frac{1}{\sqrt{2}}$$

## REVISIONARY PROBLEMS

- 2.1 Describe, in brief, the Lewis description of a covalent bond.
- 2.2 How does the Born-Oppenheimer approximation simplify the quantum mechanical treatment of the covalent bond? Explain
- 2.3 Explain, by setting the trial function of  $H_2$ , the difference between molecular orbital and valence bond methods.
- 2.4 The mixing between two orbitals depends on the following factors:
  - (i) The difference between the energies of two orbitals.
  - (ii) The extent of overlapping between them.
  - (iii) The symmetry of orbitals relative to the molecular axis.
 Justify the above factors by evaluating the energy expressions of molecular orbitals of the molecule AB.
- 2.5 Justify the following statement.  
It is often stated that the valence bond treatment of a covalent bond is very similar to the electron-pair bond postulated by Lewis.
- 2.6 Give the statement of variation theorem.
- 2.7 Derive the expressions of wave functions and the associated energies of  $H_2^+$  under the LCAO scheme of constructing molecular orbitals.
- 2.8 For  $H_2^+$ , the energies of the two wave functions are

$$E_+ - E_H = \frac{1}{R} + \frac{J + K}{1 + S_{ab}}$$

$$E_- - E_H = \frac{1}{R} + \frac{J - K}{1 - S_{ab}}$$

$$\text{where } J = -\frac{1}{R} [1 - (1 + R) \exp(-2R)]$$

$$K = -(1 + R) \exp(-2R)$$

$$S_{ab} = \left(1 + R + \frac{R^2}{3}\right) \exp(-2R)$$

and  $R$  is expressed in atomic units. Evaluate the terms  $E_+ - E_H$  at the following values of  $R$  and then draw the potential energy diagram. What do you conclude from the latter?

$R = 1.0, 1.50, 1.75, 2.00, 2.25, 2.50, 2.75, 3.00, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0$  and  $7.0$ .

- 2.9 What do you understand by (i) bonding, (ii) nonbonding, and (iii) antibonding orbitals?
- 2.10 Justify the statement that the number of molecular orbitals obtained in the LCAO is equal to the number of atomic orbitals involved in the summation.
- 2.11 Describe qualitatively the MO and VB treatments of hydrogen molecule. Compare the merits and demerits of the above two methods.

- 2.12 Draw the correlation diagram depicting the energies of various molecular orbitals relative to those of atomic orbitals in a homonuclear diatomic molecule when (i) s-p interaction is absent or small, and (ii) s-p interaction is strong. What are the shapes of these orbitals?
- 2.13 Explain the following by using the molecular orbitals of homonuclear diatomic molecules.

- (i) The bond dissociation energy of  $H_2$  is almost double that of  $H_2^+$ .
- (ii) The bond length of  $H_2$  is smaller than that of  $H_2^+$ .
- (iii)  $He_2$  is not stable but  $He_2^+$  has been observed.
- (iv)  $B_2$  and  $O_2$  are paramagnetic in nature.
- (v) The dissociation energy decreases in going from  $N_2$  to  $N_2^+$  whereas it increases in going from  $O_2$  to  $O_2^+$ .
- (vi) The dissociation energy of  $N_2$  is maximum amongst the homonuclear diatomic molecules.
- (vii) The bond length increases in going from  $N_2$  to  $N_2^+$  whereas it decreases in going from  $O_2$  to  $O_2^+$ .

- 2.14 Derive the molecular term symbol for  $H_2$ ,  $He_2^+$  and  $B_2$ .

- 2.15 (a) Draw the correlation diagram relating molecular orbitals of heteronuclear diatomic molecules AH relative to those of isolated atoms when (i) H is more electronegative than A (example LiH), and (ii) A is more electronegative than H (example HF).

- (b) How will you determine theoretically the partial ionic character in LiH bond?
- 2.16 (a) Draw the correlation diagram relating molecular orbitals of a heteronuclear diatomic molecule AB (atom B is more electronegative than A) relative to those of isolated atoms.

- (b) Write down the electronic configurations of the following molecules, BN, BO, CN,  $CO^+$ ,  $CO$ ,  $NO^+$ ,  $CN^-$  and  $NO$ .

- 2.17 What is an united-atom concept? Describe how does it lead to the correlation diagrams for homonuclear and heteronuclear diatomic molecules? What are the utilities of correlation diagrams?

- 2.18 Under the LCAO scheme, construct qualitatively the expressions and shapes of molecular orbitals involving the valence orbitals of  $BeH_2$ ,  $H_2O$  and  $CO_2$  molecules. Draw the appropriate energy diagrams and write down the electronic configurations of the above molecules.

- 2.19 (a) What are hybrid orbitals? Construct the wave functions for  $sp$ ,  $sp^2$  and  $sp^3$  hybrid orbitals. Derive the angle between the two hybrid orbitals belonging to the above categories.

- (b) Justify the statement that hybrid orbitals are better than  $p_z$  orbitals in forming the covalent bond.
- (c) Describe how the geometries of  $H_2O$ ,  $NH_4^+$ ,  $NH_3$ ,  $HC \equiv CH$ ,  $H_2C = CH_2$  and,  $H_3C - CH_3$  can be explained on the basis of hybrid orbitals.
- 2.20 (a) Describe the Hückel approximations and show how these help simplifying the LCAO-MO framework of  $\pi$ -electrons of conjugated hydrocarbons.
- (b) Derive the ground-state electronic configuration and ground-state energy for each of the following molecules: (i) ethylene, (ii) butadiene, and (iii) benzene.

- (c) Justify the statement that in the conjugated molecules, double bonds are not localized in the true sense but they are delocalized over the entire molecule.  
 (d) Define the following statements with their utilities.

- (i) Delocalization energy
- (ii) Electron density on an atom of a molecule
- (iii) Bond order
- (iv) Free valence.

- (e) Explain, how the Hückel method of conjugated hydrocarbons can be extended to heteromolecules.

2.21 Construct qualitatively the expressions of localized molecular orbitals of  $\text{BeH}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  molecules. Show that the nonlocalized bonding orbitals of these molecules can be obtained by taking 'positive' and 'negative' combinations of the appropriate localized molecular orbitals.

2.22 Construct schematically the correlation diagram depicting the change in orbital energies of the bent  $\text{AH}_2$  molecule when its bond angle is gradually increased from  $90^\circ$  to  $180^\circ$ . Derive the Walsh's rule regarding the structure of  $\text{AH}_2$  molecules.

2.23 (a) Using the Hückel approximations, show that for the allyl radical  $(\text{CH}_2-\text{CH}=\text{CH}_2)_3$ , the wave functions and the corresponding energies are given by

$$\psi_1 = \frac{1}{2} \psi_{2p_z(1)} + \frac{1}{\sqrt{2}} \psi_{2p_z(2)} + \frac{1}{2} \psi_{2p_z(3)} \quad ; \quad E_1 = \alpha + \sqrt{2}\beta$$

$$\psi_2 = \frac{1}{\sqrt{2}} \psi_{2p_z(1)} - \frac{1}{\sqrt{2}} \psi_{2p_z(3)} \quad ; \quad E_2 = \alpha$$

$$\psi_3 = \frac{1}{2} \psi_{2p_z(1)} - \frac{1}{\sqrt{2}} \psi_{2p_z(2)} + \frac{1}{2} \psi_{2p_z(3)} \quad ; \quad E_3 = \alpha - \sqrt{2}\beta$$

- (b) Show that  $\psi_1$ ,  $\psi_2$  and  $\psi_3$  are bonding, nonbonding and antibonding orbitals, respectively.

- (c) Calculate the electron densities and bond orders for (i) allyl radical, (ii) allyl cation, and (iii) allyl anion.

### TRY YOURSELF PROBLEMS

- 2.1 Write down the expression of  $H_{op}$  for the  $\text{H}_2$  molecular ion.
- 2.2 Write down the electronic configurations of  $\text{NF}^+$  and  $\text{NF}^-$ . Describe how bond energy and bond length vary in these species.
- 2.3 Discuss the bond properties of  $\text{Cl}_2$  and  $\text{Cl}_2^+$  using molecular orbital theory.
- 2.4 Explain, why the dissociation energy and bond length for  $\text{B}_2$  are greater than those for  $\text{F}_2$ ?
- 2.5 What is the ground-state configuration of  $\text{C}_2^+$ ?
- 2.6 Draw the potential energy curves for the valence bond functions of  $\text{H}_2$  from the following data expressed in atomic units:

R/atomic units	0	1	2	3	4
$S$	1.0	0.86	0.59	0.35	0.19
$\int  s_a   1/r_0   s_a  d\tau$	1.0	0.73	0.47	0.33	0.25
$\int  s_a   1/r_0   s_b  d\tau$	1.0	0.74	0.41	0.20	0.09
$\int  s_a(1)s_b(2)   1/r_{12}   s_a(1)s_b(2)  d\tau$	0.63	0.55	0.43	0.32	0.25
$1/R$	1.0	0.50	0.33	0.25	0.25

2.7 Draw the potential energy curves of  $\sigma_g$  and  $\sigma_u$  molecular orbitals of  $\text{H}_2$  molecule from the following data:

$r_{AB}/\text{bohr}$	1.00	1.50	2.00	2.50	3.00
$E(\sigma_g)/\text{hartree}$	-0.985 9	-1.097 2	-1.080 8	-1.033 8	-0.982 9
$E(\sigma_u)/\text{hartree}$	+0.705 2	+0.057 9	-0.274 6	-0.462 8	-0.575 0
	3.50	5.00	7.00		
	-0.935 8	-0.834 3	-0.770 8		
	-0.643 8	-0.729 1	-0.746 4		

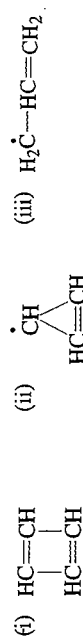
Compute the values of bond distance and bond energy.

2.8 Describe the molecular orbital treatment of the molecular ion  $\text{HeH}^+$  relative to that  $\text{H}_2$ .

2.9 Is the allene molecule  $\text{CH}_2=\text{C}=\text{CH}_2$  belong to conjugated molecule?

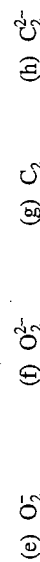
2.10 The molecule  $\text{CH}_2$  is nonlinear with bond angle near to  $180^\circ$ . Experimentally, this molecule is found to be triplet and not the singlet as is expected from the correlation diagram of bent  $\text{AH}_2$  molecule. How will you explain this behaviour?

2.11 Calculate the delocalization energy of the following:



[Ans. (i) zero (ii)  $\beta$  and (iii)  $0.828\beta$ ]  
 2.12 Explain why  $\text{O}_2^-$  has a longer bond than  $\text{O}_2$  (0.121 nm versus 0.112 nm) whereas  $\text{CN}^-$  has a shorter bond than  $\text{CN}$  (0.109 nm versus 0.118 nm).

2.13 Which of the following species would you expect to be paramagnetic?



2.14 Show that for a linear polyene containing  $2N$  carbon atoms, the longest  $\pi \rightarrow \pi^*$  transition is given by the expression

$$\Delta E = -4\beta \sin \left( \frac{\pi}{2(2N+1)} \right)$$

- 2.15 Using the Hückel parameters  $h_0 = 1$  and  $k_{C=O} = 1.1$ , derive the ground-state energy for the system  $\text{>C=O}$  and compare it with that of  $\text{>C=C<}$

- 2.16 Explain why:

- (a)  $\text{N}_2$  and  $\text{I}_2$  are diamagnetic.  
(b)  $\text{C}_2$  is paramagnetic.

- 2.17 Which of the species  $\text{N}_2$ ,  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{C}_2$ ,  $\text{F}_2$ ,  $\text{CN}$  would you expect to be stabilized by the (a) addition of an electron, (b) removal of an electron?

[Ans. (a)  $\text{C}_2$ ,  $\text{CN}$ ; (b)  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{F}_2$ ]

- 2.18 Arrange the following molecules in order of increasing bond length:  $\text{O}_2$ ,  $\text{O}_2^+$ ,  $\text{O}_2^-$  and  $\text{O}_2^{2-}$ . Which molecule will have the greater dissociation energy:  $\text{O}_2$  or  $\text{O}_2^+$ ?

[Ans.  $\text{O}_2^+ < \text{O}_2 < \text{O}_2^- < \text{O}_2^{2-}$ ;  $\text{O}_2^+ > \text{O}_2$ ]

- 2.19 Rationalize the empirical facts that the ionization energy of  $\text{H}_2$  is greater than that of atomic H, whereas that of  $\text{O}_2$  is less than that of atomic O.

- 2.20 Would you expect  $\text{Cl}_2^-$  to exist as a stable species? Why?

- 2.21 Explain whether the molecules  $\text{PH}_3$ ,  $\text{PF}_3$ ,  $\text{SO}_2$  and  $\text{MgH}_2$  should be bent or linear.

- 2.22 (a) Construct molecular orbitals of  $\text{MgF}_2$  (linear structure) starting from 3s and 3p orbitals of Mg and 2s and 2p orbitals of F. Write down its electronic configuration.  
(b) Write down the electronic configuration of  $\text{NH}_2^-$ .

- 2.23 Draw the molecular orbital diagram for (a) CO and (b) XeF and write their electronic configurations. Show that  $\text{XeF}^+$  is more stable than XeF.

- 2.24 For linear  $\text{H}_3$  molecule, three molecular orbitals formed from three 1s orbitals are given by

$$\psi_1 = C_1\psi_{1s(\text{H}_a)} + C_2\psi_{1s(\text{H}_b)} + C_3\psi_{1s(\text{H}_c)}$$

$$\psi_2 = C_4\psi_{1s(\text{H}_a)} - C_5\psi_{1s(\text{H}_c)}$$

$$\psi_3 = C_6\psi_{1s(\text{H}_a)} - C_7\psi_{1s(\text{H}_b)} + C_8\psi_{1s(\text{H}_c)}$$

The orbital  $\psi_1$  is strongly bonding,  $\psi_2$  is weakly antibonding between the end atoms and nonbonding between the outer and centre atoms and  $\psi_3$  is strongly antibonding. Justify the following facts.

- (i)  $\text{H}_3$  is stable with respect to 3H.  
(ii)  $\text{H}_3$  is slightly unstable with respect to  $\text{H}_2$  and H and thus  $\text{H}_3$  is a transient species and cannot be isolated in large amount.  
(iii) The geometry of  $\text{H}_3$  is linear because of the presence of one electron in  $\psi_2$  which is antibonding between the two end atoms.  
(iv)  $\text{H}_3^+$  is stable with respect to (i)  $\text{H}^+ + 2\text{H}$  and (ii)  $\text{H}^+$  and  $\text{H}_2$ .  
(v) The geometry of  $\text{H}_3^+$  is not linear but an equilateral triangle.  
(vi) Consider the  $\text{H}_3^+$  molecule in both the linear  $(\text{H}-\text{H}-\text{H})^+$  and triangular

$\left( \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{H}-\text{H} \end{array} \right)^+$  states. Utilizing simple Hückel approximations with the

hydrogen 1s orbitals as a basis set, set up the secular determinant and compute the energies of the molecular orbitals for each geometry. Predict which geometry would be more stable for  $\text{H}_3^+$  and  $\text{H}_3$ .

[Ans. (i) Because of two electrons in strongly bonding orbital, (ii) because of one electron in weakly antibonding orbital, (iii) any bending of the molecule brings two end atoms together which is opposed by the electron in the weakly antibonding orbital, (iv) no electron in antibonding orbital, and (v) electrons are present only in bonding orbital between the end atoms and is formed by mutual overlap of three 1s atomic orbitals.]

- 2.25 Justify the following facts by making use of Fig. 2.15.1.

- (a)  $\text{BH}_2$  is bent in ground state and is linear in the first electronically excited state.  
(b)  $\text{NH}_2$  is bent in both ground and first electronically excited state.  
(c)  $\text{H}_2\text{O}$  molecule is bent in the ground state.

- 2.26 Using Walsh' rules, predict the geometries of the following molecules: (a) CCO, (b) FCO, (c) NCO, (d) FOO, (e) FCN, (f) FNO, (g) OBO, (h) CNC, (i)  $\text{O}_3^+$  and (k)  $\text{F}_3^+$ .

- 2.27 HCN is a linear molecule. Construct the two localized MOs and then transform them into nonlocalized MOs. Draw the correlation diagram and write the electronic configuration of HCN.

- 2.28 Given below are the computed values of  $J$ ,  $K$ ,  $S_{AB}$ ,  $E_+$  and  $E_-$  and  $E_+$  at the various values of  $R$  of  $\text{H}_2^+$  molecule. Plot  $E_+$  -  $E_H$  versus  $R$  and  $E_-$  -  $E_H$  versus  $R$  and compare them with those given in Fig. 2.5.3.

$R$ atomic unit	$J/\text{hartree}$ (Eq. 2.5.25)	$K/\text{hartree}$ (Eq. 2.5.26)	$S_{AB}$ (Eq. 2.5.27)	$(E_+ - E_H)/$ hartree (Eq. 2.5.24a)	$(E_- - E_H)/$ hartree (Eq. 2.5.24b)
1.0	-0.729	-0.736	0.858	0.212	1.045
1.25	-0.652	-0.645	0.794	0.077	0.763
1.5	-0.584	-0.558	0.725	0.005	0.573
1.75	-0.524	-0.478	0.655	-0.034	0.438
2.0	-0.473	-0.406	0.586	-0.054	0.339
2.5	-0.391	-0.287	0.458	-0.065	0.210
3.0	-0.330	-0.199	0.349	-0.059	0.133
3.5	-0.285	-0.136	0.244	-0.052	0.089
4.0	-0.250	-0.092	0.189	-0.037	0.055
4.5	-0.222	-0.061	0.136	-0.027	0.036
5.0	-0.199	-0.040	0.096	-0.019	0.024
5.5	-0.182	-0.027	0.068	-0.013	0.015
6.0	-0.167	-0.015	0.053	-0.006	0.006
7.0	-0.143	-0.006	0.028	-0.002	0.003

- 2.29 The  $\text{N}_3^+$  molecule has a linear structure. Construct the localized and nonlocalized orbitals and draw their contour diagrams. Is it diamagnetic or paramagnetic?

- 2.30 The molecule CO is written as :C≡O: with C as the negative end of the dipole. Explain this structure on the basis of MO theory and also explain the fact that CO is a better electron pair donor through carbon.

(Hint: See Annexure I at the end of the chapter for MO treatment of CO.)

- 2.31 Derive the molecular term symbols for the ground state of  $\text{H}_2^+$ ,  $\text{C}_2$ ,  $\text{N}_2^+$ ,  $\text{N}_2$ ,  $\text{O}_2^+$ ,  $\text{O}_2$  and  $\text{F}_2$ .

- 2.32 (a) The four lowest molecular orbitals of water molecule are as follows.

$$[\text{Ans. } ^2\Sigma, ^1\Sigma, ^2\Sigma, ^1\Sigma, ^2\Pi, ^3\Sigma \text{ and } ^1\Sigma]$$

$$\psi_1 = 0.820\psi_{2s(\text{O})} + 0.132\psi_{p_z(\text{O})} + 0.152[\psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)}]$$

$$\psi_2 = 0.441[\psi_{2p_x(\text{O})} + \psi_{2p_x(\text{O})}] + 0.424[\psi_{1s(\text{H}_a)} - \psi_{1s(\text{H}_b)}]$$

$$\psi_3 = 0.502\psi_{2s(\text{O})} - 0.787\psi_{2p_z(\text{O})} - 0.264[\psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)}]$$

$$\psi_4 = 0.707[\psi_{2p_x(\text{O})} - \psi_{2p_x(\text{O})}]$$

$$\text{If } S[\psi_{1s(\text{H}_a)}, 2s(\text{O})] = S[\psi_{1s(\text{H}_b)}, 2s(\text{O})] = 0.471$$

$$S[\psi_{1s(\text{H}_a)}, 2p_x(\text{O})] = -S[\psi_{1s(\text{H}_b)}, 2p_x(\text{O})] = 0.225$$

$$S[\psi_{1s(\text{H}_a)}, 2p_y(\text{O})] = -S[\psi_{1s(\text{H}_b)}, 2p_y(\text{O})] = 0.225$$

$$S[\psi_{1s(\text{H}_a)}, 2p_z(\text{O})] = S[\psi_{1s(\text{H}_b)}, 2p_z(\text{O})] = 0.247$$

$$S[\psi_{1s(\text{H}_a)}, \psi_{1s(\text{H}_b)}] = 0.238$$

Calculate Mulliken gross atomic population numbers of atoms.

- (b) What would be the molecular orbitals if the charge densities on atoms under zero-overlap approximation are equal to the corresponding atomic population numbers calculated in part (a) of the question?

[Ans. (a) 6.446 on oxygen and 0.777 on each hydrogen.

$$(b) \psi_1 = 0.889[\psi_{2s(\text{O})} + 0.165\psi_{2p_z(\text{O})} + 0.303(\psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)})]$$

$$\psi_2 = 0.528[\psi_{2p_x(\text{O})} + \psi_{2p_x(\text{O})}] + 0.470[\psi_{1s(\text{H}_a)} - \psi_{1s(\text{H}_b)}]$$

$$\psi_3 = 0.357\psi_{2s(\text{O})} - 0.849\psi_{2p_z(\text{O})} - 0.274[\psi_{1s(\text{H}_a)} + \psi_{1s(\text{H}_b)}]$$

$$\psi_4 = 0.707[\psi_{2p_x(\text{O})} - \psi_{2p_x(\text{O})}]$$

## ANNEXURE I

### Localized Molecular Orbitals of CO and $\text{N}_2$ Molecules

#### INTRODUCTION

A large number of complex compounds of carbon monoxide with the transition metals are known. In these molecules, the linkage between the two is through the carbon end of the CO molecule. This is due to the presence of a lone pair of electrons on carbon which can be easily shared between its orbital and the empty d orbital of the transition metal. Though the oxygen end of the CO molecule also contains a lone pair of electrons, yet no compound is known where this lone pair of electrons is involved. Similarly, the molecule  $\text{N}_2$ , which is isoelectronic to CO, is essentially behaves like an inert molecule. In order to understand these characteristics, it is worth considering the electronic structures of these two molecules from the viewpoint of their molecular orbitals and their associated directional characteristics.

The general appearances of the correlation diagrams of  $\text{N}_2$  and CO molecules will be very similar to those described by Figs 2.9.4, and 2.11.3, respectively. The contour diagrams of the associated molecular orbitals will also be very similar to those described by Figs 2.9.1 and 2.11.4, respectively. The great difference in their ligand characteristics are not brought out specifically by these nonlocalized molecular orbitals. However, these characteristics are better understood from the correlation diagrams involving the localized molecular orbitals as proposed by Jaffe and Orchin. Before describing these diagrams, it is desirable to understand qualitatively the classical description of the chemical bonds existing in the above two molecules.

#### NITROGEN MOLECULE

The electronic configuration of N atom is  $(1s)^2(2s)^2(2p_x)^1(2p_y)^1(2p_z)^1$ . It contains three unpaired electrons. The  $\text{N}_2$  molecule is diamagnetic indicating the absence of any unpaired electrons. This indicates the presence of a triple bond between the two N atoms. This triple bond will include one  $\sigma$  bond (formed by the overlapping of  $2p_z$  atomic orbitals) and two  $\pi$  bonds (formed by the side way overlapping of  $2p_x(\text{N}_A)$  with  $2p_x(\text{N}_B)$  and  $2p_y(\text{N}_A)$  with  $2p_y(\text{N}_B)$  atomic orbitals, respectively. Each atom is expected to possess a lone pair of 2s electrons with no directional characteristics. For better overlapping of orbitals, a little sp hybridization may be involved subject to the minimization of electronic energy. Thus  $\sigma$  bond may be considered to involve  $sp_1(\text{N}_A)$  and  $sp_1(\text{N}_B)$  orbitals, where each of these orbitals involves the larger contribution from the  $2p_z$  orbital and lesser from the 2s orbital. The lone pairs will be present in  $sp_2(\text{N}_A)$  and  $sp_2(\text{N}_B)$ , each of which involves the major contribution from the respective 2s orbital and lesser from the  $2p_z$  orbital and thus are essentially nondirectional.

#### Description of Bonding



## Description of Bonding

### CARBON MONOXIDE

The electronic configuration of C and O are  $(1s)^2(2s)^2(2p_x)^1(2p_y)^1$  and  $(1s)^2(2s)^2(2p_x)^2(2p_y)^1$ , respectively. In order to understand the directional characteristics of a lone pair of electrons on C atom, the arrangement of its valence electrons may be assumed to be as follows.



where  $sp_1$  and  $sp_2$  are the two hybrid orbitals formed from the  $2s$  and  $2p_z$  orbitals of carbon. This hybridization may be either complete (equal percentage of orbitals) or partial (unequal percentage) dependent upon the minimization of electronic energy. In the CO molecule, the presence of two  $\pi$  bonds may be proposed due to the side-way overlapping of  $2p_x(C)$  with  $2p_x(O)$  and  $2p_y(C)$  with  $2p_y(O)$  orbitals, respectively. Besides these, a third bond may exist due to the overlapping of the  $sp_2(C)$  orbital with the  $2p_z(O)$  orbital and the two electrons in this bond come exclusively from the O atom. In classical view-point, this bond is known as the coordinate bond. Hence, we may write the molecule CO as



where the lone pairs on C and O will be present in  $sp_1(C)$  and  $2s(O)$  orbitals, respectively. The electrons on the C atom are expected to possess directional characteristics whereas those present on the O atom are expected to be non-directional. For better overlapping,  $2s(O)$  and  $2p_z(O)$  may be assumed to involve partial  $sp$  hybridization. The hybrid orbital involving the larger contribution from the  $2p_z(O)$  orbital is expected to form the coordinate bond whereas the other one having larger contribution from  $2s(O)$  will possess the lone pair of electrons.

The dipole moment of CO is 0.118 D, a small value with carbon as the negative end of the dipole. Qualitatively, this fact may be rationalized on the basis of the above proposed structure of carbon monoxide. Since the oxygen atom is more electronegative than the carbon atom, the electrons in the  $\pi$ -bonds will be more near to the oxygen atom. Consequently, the oxygen atom will acquire a net  $\delta^-$ -charge and carbon a net  $\delta^+$ -charge. This drift of electronic charge is more than counteracted by the mutual sharing of the two electrons of oxygen atom in the coordinate bond resulting in the net  $\delta^-$ -overall charge on carbon and  $\delta^+$ -overall charge on oxygen.

The proposed structures of  $N_2$  and CO can also be explained from the correlation diagrams involving the localized molecular orbitals. These were proposed by Jaffe and Orchin and are described below.

## Correlation Diagram of Nitrogen

As usual, the energy of valence orbitals of isolated atoms are depicted at the extreme right and left of the correlation diagram (Fig. A.1a). The  $2s$  and  $2p_z$  orbitals on each atom form partial  $sp$  hybridization according to the expressions:

$$\begin{aligned}\psi_{sp_1}(N_A) &= \psi_{2s}(N_A) - \lambda \psi_{2p_z}(N_A) \\ \psi_{sp_2}(N_A) &= \lambda \psi_{2s}(N_A) + \psi_{2p_z}(N_A)\end{aligned}$$

$$\begin{aligned}\psi_{sp_1}(N_B) &= \psi_{2s}(N_B) - \lambda \psi_{2p_z}(N_B) \\ \psi_{sp_2}(N_B) &= \lambda \psi_{2s}(N_B) + \psi_{2p_z}(N_B)\end{aligned}$$

where  $\lambda$  is the weighing factor†.

The hybrid orbitals  $sp_1(N_A)$  and  $sp_1(N_B)$  include more contribution from the respective  $2s(N)$  orbitals and will have energies slightly larger than the respective  $2s(N)$  orbitals††. Because of the larger contribution from  $2s(N)$  orbitals, the hybrid orbitals do not possess much of the directional characteristics and thus will act as nonbonding orbitals.

The hybrid orbitals  $sp_2(N_A)$  and  $sp_2(N_B)$  include more contribution from the respective  $2p_z(N)$  orbitals and will have energies slightly smaller than the respective  $2p_z(N)$  orbitals. Because of the larger contribution from  $2p_z(N)$  orbitals, the hybrid orbitals will possess directional characteristics along the N—N axis. From these two orbitals, two localized molecular orbitals (bonding and antibonding) will be formed according to the expressions†:

$$\psi_1 = C_1(\psi_{sp_2}(N_A) - \psi_{sp_2}(N_B)); \quad (\text{bonding})$$

$$\psi_1' = C_1'(\psi_{sp_2}(N_A) + \psi_{sp_2}(N_B)); \quad (\text{antibonding})$$

The  $2p_x$  and  $2p_y$  orbitals centred on each of the two nitrogen atoms will form doubly degenerate  $\pi$  and  $\pi^*$  molecular orbitals according to the expressions given below.

$$\psi_2 = C_2(\psi_{2p_x}(N_A) + \psi_{2p_x}(N_B)); \quad (\text{bonding})$$

$$\psi_3 = C_2'(\psi_{2p_x}(N_A) - \psi_{2p_x}(N_B)); \quad (\text{bonding})$$

$$\psi_2' = C_3(\psi_{2p_x}(N_A) - \psi_{2p_x}(N_B)); \quad (\text{antibonding})$$

$$\psi_3' = C_3'(\psi_{2p_x}(N_A) + \psi_{2p_x}(N_B)); \quad (\text{antibonding})$$

The energies of bonding orbitals  $\psi_2$  and  $\psi_3$  will be smaller than those of  $2p(N_A)$  and  $2p(N_B)$ , whereas those of antibonding orbitals  $\psi_2'$  and  $\psi_3'$  will be larger than the energies of these orbitals. Similarly, the bonding molecular orbitals  $\psi_1$  will be more stable than  $sp_2(N_A)$  and  $sp_2(N_B)$  and the antibonding orbital  $\psi_1'$  will be less stable than these hybrid atomic orbitals. Since end to end overlap is larger than side way overlap, the bonding  $\sigma$  orbital  $\psi_1$  will be more stable than the bonding  $\pi$

† The weighing factor would be unnecessary if the hybrid orbitals were made up of equal parts of  $s$  and  $p$ , but one orbital ( $sp_1$ ) has more  $s$  than  $p$  character, and the other ( $sp_2$ ) less  $s$  than  $p$  character ( $0 \leq \lambda \leq 1$ ).

†† According to the advanced calculations by Scherr's, the  $2s$  contribution is about 71 per cent.

† The symmetry of the molecule requires that each molecular orbital will be made up of equal contributions from the two atoms.



orbitals  $\psi_2$  and  $\psi_3$ . On the other hand, the antibonding  $\sigma$  orbital  $\psi'_1$  will be less stable than the antibonding  $\pi$  orbitals  $\psi'_2$  and  $\psi'_3$ .

Figure A1.1a depicts the expected energy level diagram for the  $N_2$  molecule. Its electronic configuration will be

$$(\psi_1)^2, (\psi_{sp_1(N_A)})^2, (\psi_{sp_1(N_B)})^2, (\psi_2)^2, (\psi_3)^2$$

The molecule will have a triple bond; one  $\sigma$  bond due to the two electrons in  $\psi_1$ ; and two  $\pi$  bonds due to the two electrons in each of  $\psi_2$  and  $\psi_3$  molecular orbitals. The two electrons in each of  $\psi_{sp_1(N_A)}$  and  $\psi_{sp_1(N_B)}$  will constitute two lone pairs of electrons, essentially of 2s character with not much of the directional characteristics. It is because of this fact that the  $N_2$  molecule does not exhibit any complex-compound formation with the transition metals.

### Correlation Diagram of Carbon Monoxide

The energies of valence orbitals of C and O are:

$$E_{2s(C)} \approx -1.88 \text{ MJ mol}^{-1}$$

$$E_{2p(C)} \approx -1.03 \text{ MJ mol}^{-1}$$

$$E_{2s(O)} \approx -3.13 \text{ MJ mol}^{-1}$$

$$E_{2p(O)} \approx -1.53 \text{ MJ mol}^{-1}$$

The placing of these energies at the extreme right and left of the correlation diagram is not symmetrical (Fig. A.1b).

The difference in energies of  $2s(C)$  and  $2p(C)$  orbitals is smaller than that exists between  $2s(O)$  and  $2p(O)$  orbitals. This feature plays a predominant role in the effective mixing of  $2s$  and  $2p_z$  orbitals to form  $sp$  hybrid orbitals. The mixing in case of C is expected to be more as the difference in energy levels of the involved orbitals is less. The hybrid orbitals will be given by the expressions:

$$\psi_{sp_1(C)} = \psi_{2s(C)} + \lambda \psi_{2p_z(C)}$$

$$\psi_{sp_2(C)} = \lambda' \psi_{2s(C)} - \psi_{2p_z(C)}$$

$$\psi_{sp_1(O)} = \psi_{2s(O)} + \lambda' \psi_{2p_z(O)}$$

$$\psi_{sp_2(O)} = \lambda' \psi_{2s(O)} - \psi_{2p_z(O)}$$

with  $\lambda' < \lambda$ .<sup>†</sup> Energy of  $sp_1(C)$  will be larger than that of its predominant atomic orbital, i.e.  $2s(C)$  whereas that of  $sp_2(C)$  will be smaller than that of its predominant atomic orbital, i.e.  $2p_z(C)$ . Similarly,  $sp_1(O)$  and  $sp_2(O)$  will lie, respectively, above and below of  $2s(O)$  and  $2p_z(O)$  atomic orbitals.

<sup>†</sup> According to the advanced calculations by Sahni,  $sp_1(C)$  and  $sp_1(O)$  include about 32 and 22 per cents  $p$  character, respectively. On the other hand,  $sp_2(C)$  and  $sp_2(O)$  include about 32 and 22 per cents  $s$  character, respectively.

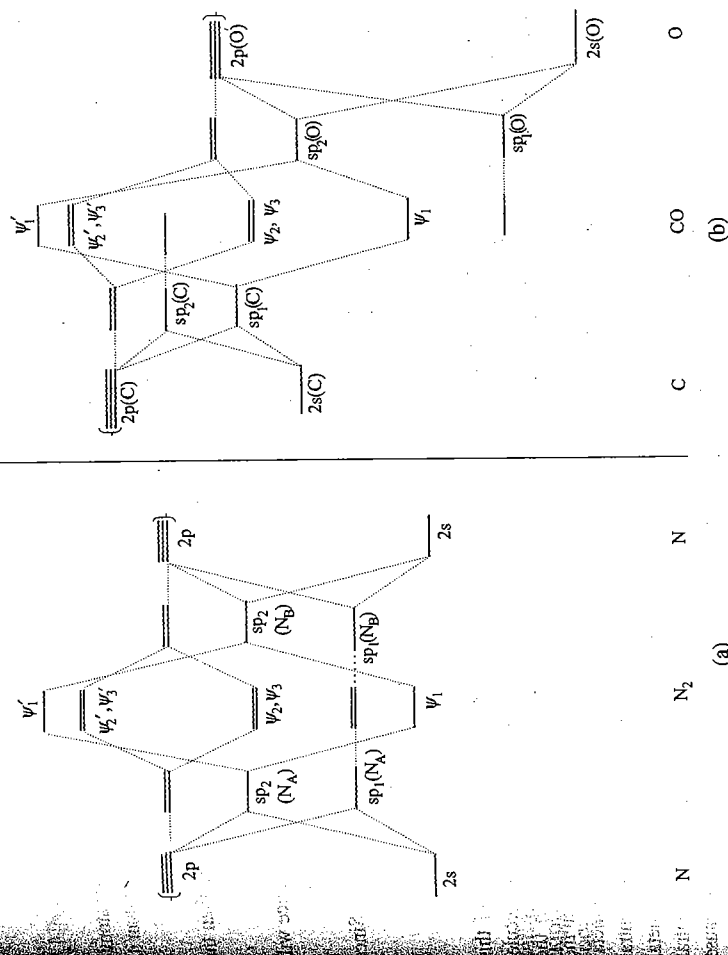


Fig. A1.1 Correlation diagram of the (a) nitrogen, and (b) carbon monoxide molecules

From Fig. A1.1b, it may be seen that the energy of  $2p(O)$  orbital lies in between those of  $2s(C)$  and  $2p(C)$ . Consequently, the energy of the  $sp_2(O)$  orbital lies near to that of the  $sp_1(C)$  orbital rather than that of  $sp_2(C)$  orbital. It is thus expected that the  $\sigma$  bond formation between C and O is due to the involvement of  $sp_1(C)$  and  $sp_2(O)$  orbitals. Hence we may write

$$\psi_1 = C_1 \psi_{sp_1(C)} + C_2 \psi_{sp_2(O)}; \quad (\text{bonding}, C_2 > C_1)^\dagger$$

$$\psi'_1 = C'_1 \psi_{sp_1(C)} - C'_2 \psi_{sp_2(O)}; \quad (\text{antibonding}, C'_1 > C'_2)^\dagger$$

The  $2p_x$  and  $2p_y$  orbitals centred on each of the two atoms will form doubly degenerate  $\pi$  and  $\pi^*$  molecular orbitals as in the case of nitrogen molecule according to the expressions given below.

$$\psi_2 = C_3 \psi_{2p_x(C)} + C_4 \psi_{2p_x(O)}; \quad (\text{bonding}, C_4 > C_3)$$

$$\psi_3 = C_5 \psi_{2p_y(C)} + C_6 \psi_{2p_y(O)}; \quad (\text{bonding}, C_6 > C_5)$$

<sup>†</sup> The terms  $C_2 > C_1$  and  $C'_1 > C'_2$  follow from the fact that the electron density in the bonding orbital will be more on the more electronegative atom whereas in the antibonding orbital, it is more on the lesser electronegative atom.

$$\begin{aligned}\psi_2 &= C_3' \psi_{2p_x(\text{C})} - C_4' \psi_{2p_x(\text{O})}; & (\text{antibonding, } C_3' > C_4') \\ \psi_3 &= C_5' \psi_{2p_y(\text{C})} - C_6' \psi_{2p_y(\text{O})}; & (\text{antibonding, } C_5' > C_6')\end{aligned}$$

The orbitals  $\psi_2$  (or  $\psi_3$ ) will be more stable than its more stable constituent atomic orbital  $2p_y(\text{O})$  (or  $2p_x(\text{O})$ ), whereas the orbital  $\psi_2'$  (or  $\psi_3'$ ) will be less stable than its lesser stable constituent atomic orbital  $2p_x(\text{C})$  (or  $2p_y(\text{C})$ ).

The antibonding  $\sigma$  orbital  $\psi_1'$ , as usual, is expected to be less stable than the antibonding  $p$  orbitals  $\psi_2'$  and  $\psi_3'$ .

The  $sp_2(\text{C})$  and  $sp_1(\text{O})$  do not take part into the bond formation and hence will act as nonbonding orbitals.

Figure A.1b depicts the expected correlation diagram of the CO molecule. Since the latter has 10 valence electrons, its electronic configuration will be

$$(\psi_{sp_1(\text{O})})^2 (\psi_1')^2 (\psi_2')^2 (\psi_3')^2 (\psi_{sp_2(\text{O})})^2$$

The correlation diagram of the CO molecule explains nicely the ability of this molecule to form transition metal complexes through the carbon end of the molecule. The highest occupied molecular orbital is the nonbonding orbital with the predominant  $2p$  character of the carbon. This orbital is mainly concentrated on the side of the carbon remote from the oxygen. This orbital can overlap with a metal orbital to form a sigma bond. The attachment of carbonyl groups with the central metal places substantial negative charge on the metal. This charge on the metal can be relieved by donation of electrons from  $d_{xy}$ ,  $d_x$  and  $d_z$  orbitals of the central metal to the lowest unoccupied  $\pi$  orbital of the CO molecule. This happens because of the fact that  $d_{xy}$  (or  $d_x$  or  $d_z$ ) orbital has the same appearances as that of the lowest unoccupied orbital and thus results into a positive overlap. This is known as *back bonding*. The sharing of two electrons of  $sp_2(\text{C})$  of the CO molecule with the metal atom and the back-bonding in the antibonding orbital of the CO molecule result into the weakening of the C—O bond. Consequently, the force constant of C—O bond decreases which, in turn, results into a decrease in the bond stretching frequency as is evident from infrared spectra of the unbounded and bounded CO molecules.

## Ligand Characteristics of Carbon Monoxide

## ANNEXURE II

### Evaluation of Integrals $J$ , $K$ and $S$ in the LCAO-MO treatment of $\text{H}_2^+$

The integrals  $J$ ,  $K$  and  $S$  in the LCAO-MO treatment of  $\text{H}_2^+$  are:

$$J = \left\langle \psi_{1s(\text{A})} \left| -\frac{e^2}{(4\pi\epsilon_0)r_{\text{B}}} \right| \psi_{1s(\text{A})} \right\rangle \quad (\text{AII.1})$$

$$K = \left\langle \psi_{1s(\text{A})} \left| -\frac{e^2}{(4\pi\epsilon_0)r_{\text{A}}} \right| \psi_{1s(\text{B})} \right\rangle \quad (\text{AII.2})$$

$$S = \langle \psi_{1s(\text{A})} | \psi_{1s(\text{B})} \rangle \quad (\text{AII.3})$$

These integrals involving two centres A and B at a fixed distance can be evaluated by using confocal elliptical coordinates defined as

$$\mu = \frac{r_{\text{A}} + r_{\text{B}}}{R} \quad (\text{AII.4})$$

$$\nu = \frac{r_{\text{A}} - r_{\text{B}}}{R} \quad (\text{AII.5})$$

and the angle  $\phi$  which is the angle between the plane passing through all the three particles (two nuclei and one electron) and the fixed plane  $xz$  passing through the two nuclei. The range of these variables is

$$1 \leq \mu \leq \infty \quad (\text{AII.6})$$

$$-1 \leq \nu \leq +1 \quad (\text{AII.7})$$

$$0 \leq \phi \leq 2\pi \quad (\text{AII.8})$$

The volume element  $dv$  in terms of elliptical coordinates is given by

$$dv = \frac{R^3}{8} (\mu^2 - \nu^2) d\mu d\nu d\phi \quad (\text{AII.9})$$

The atomic wave functions  $\psi_{1s(\text{A})}$  and  $\psi_{1s(\text{B})}$  are

$$\psi_{1s(\text{A})} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr_{\text{A}}/a_0} \quad (\text{AII.10})$$

$$\psi_{1s(\text{B})} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr_{\text{B}}/a_0} \quad (\text{AII.11})$$

### Atomic Orbitals Expressed in Atomic Units

In terms of atomic units, these are expressed as

$$\psi_{1s(A)} = \frac{1}{\sqrt{\pi}} e^{-r_A} \quad (\text{where } Z=1) \quad (\text{AII.12})$$

$$\psi_{1s(B)} = \frac{1}{\sqrt{\pi}} e^{-r_B} \quad (\text{where } Z=1) \quad (\text{AII.13})$$

The integral  $J$  in atomic units is given by

$$J = \left\langle \frac{1}{\sqrt{\pi}} e^{-r_A} \left| \frac{1}{r_B} \frac{1}{\sqrt{\pi}} e^{-r_A} \right| \right\rangle = -\frac{1}{\pi} \int e^{-2r_A} \cdot \frac{1}{r_B} d\tau \quad (\text{AII.14})$$

From the expressions  $\mu = (r_A + r_B)/R$  and  $v = (r_A - r_B)/R$ , we get

$$\mu + v = 2r_A/R \quad \text{and} \quad \mu - v = 2r_B/R$$

With these, Eq. (AII.14) becomes

$$J = -\frac{1}{\pi} \int e^{-R(\mu+v)} \cdot \frac{1}{R(\mu-v)/2} d\tau$$

Substituting  $d\tau$  from Eq. (AII.9), we get

$$J = -\frac{1}{\pi} \int e^{-R(\mu+v)} \cdot \frac{1}{R(\mu-v)/2} \cdot \frac{R^3}{8} (\mu^2 - v^2) d\mu dv d\phi$$

$$= -\frac{R^2}{4\pi} \int e^{-R(\mu+v)} (\mu + v) d\mu dv d\phi$$

$$\begin{aligned} &= -\frac{R^2}{4\pi} \left[ \int_1^\infty \mu e^{-R\mu} d\mu \int_{-1}^{+1} \int_0^{2\pi} e^{-Rv} dv \int_0^{2\pi} d\phi + \int_1^\infty e^{-R\mu} d\mu \int_{-1}^{+1} v e^{-Rv} dv \int_0^{2\pi} d\phi \right] \\ &= -\frac{R^2}{2} \left[ \int_1^\infty \mu e^{-R\mu} d\mu \int_{-1}^{+1} e^{-Rv} dv + \int_1^\infty e^{-R\mu} d\mu \int_{-1}^{+1} v e^{-Rv} dv \right] \quad (\text{AII.15}) \end{aligned}$$

Carrying out the integration by parts, we have

$$\begin{aligned} \int_1^\infty \mu e^{-R\mu} d\mu &= \left[ \mu \frac{e^{-R\mu}}{-R} - \frac{e^{-R\mu}}{(-R)^2} \right]_1^\infty = \left( \frac{1}{R} + \frac{1}{R^2} \right) e^{-R} \\ \int_{-1}^{+1} e^{-Rv} dv &= \left[ \frac{e^{-Rv}}{-R} \right]_{-1}^{+1} = -\frac{e^{-R}}{R} + \frac{e^R}{R} = \frac{1}{R} (e^R - e^{-R}) \\ \int_1^\infty e^{-R\mu} d\mu &= \left[ \frac{e^{-R\mu}}{-R} \right]_1^\infty = -\frac{e^{-R}}{R} \\ \int_{-1}^{+1} v e^{-Rv} dv &= \left[ v \frac{e^{-Rv}}{-R} - \frac{e^{-Rv}}{(-R)^2} \right]_{-1}^{+1} = -\left( \frac{1}{R} + \frac{1}{R^2} \right) e^{-R} + \left( \frac{1}{R} + \frac{1}{R^2} \right) e^R \end{aligned}$$

Substituting these integrals in Eq. (AII.15) and simplifying, we get

$$J = -\frac{1}{R} [1 - (1 + R)e^{-2R}] \quad (\text{AII.16})$$

The integral  $K$  in atomic units is given by

$$\begin{aligned} K &= \left\langle \frac{1}{\sqrt{\pi}} e^{-r_A} \left| \frac{1}{r_A} \frac{1}{\sqrt{\pi}} e^{-r_B} \right| \right\rangle \\ &= -\frac{1}{\pi} \int e^{-(r_A + r_B)} \cdot \frac{1}{r_A} d\tau \\ &= -\frac{1}{\pi} \int e^{-R\mu} \cdot \frac{2}{R(\mu + v)} \cdot \frac{R^3}{8} (\mu^2 - v^2) d\mu dv d\phi \\ &= -\frac{R^2}{4\pi} \int e^{-R\mu} (\mu - v) d\mu dv d\phi \\ &= -\frac{R^2}{4\pi} \left[ \int_1^\infty \mu e^{-R\mu} d\mu \int_{-1}^{+1} \int_0^{2\pi} d\phi - \int_1^\infty e^{-R\mu} d\mu \int_{-1}^{+1} v dv \int_0^{2\pi} d\phi \right] \\ &= -\frac{R^2}{4\pi} \left[ \left( \frac{1}{R} + \frac{1}{R^2} \right) e^{-R} (2)(2\pi) - \left( \frac{e^{-R}}{R} \right) (0)(2\pi) \right] \\ &= -(1 + R)e^{-R} \quad (\text{AII.17}) \end{aligned}$$

The integral  $S$  in atomic units is given by

$$\begin{aligned} S &= \left\langle \frac{1}{\pi} e^{-r_A} \left| \frac{1}{\pi} e^{-r_B} \right| \right\rangle = \frac{1}{\pi} \int e^{-(r_A + r_B)} d\tau \\ &= \frac{1}{\pi} \int e^{-R\mu} \cdot \frac{R^3}{8} (\mu^2 - v^2) d\mu dv d\phi \\ &= \frac{R^3}{8\pi} \left[ \int_1^\infty \mu^2 e^{-R\mu} d\mu \int_{-1}^{+1} \int_0^{2\pi} d\phi - \int_1^\infty e^{-R\mu} d\mu \int_{-1}^{+1} v^2 dv \int_0^{2\pi} d\phi \right] \end{aligned}$$

Now

$$\begin{aligned} \int_1^\infty \mu^2 e^{-R\mu} d\mu &= \left[ \mu^2 \frac{e^{-R\mu}}{(-R)} - 2\mu \frac{e^{-R\mu}}{(-R)^2} + \frac{e^{-R\mu}}{(-R)^3} \right]_1^\infty \\ &= \left( \frac{1}{R} + \frac{2}{R^2} + \frac{2}{R^3} \right) e^{-R} \end{aligned}$$

$$\begin{aligned} \text{Hence, } S &= \frac{R^3}{8\pi} \left[ \left\{ \left( \frac{1}{R} + \frac{2}{R^2} + \frac{2}{R^3} \right) e^{-R} \right\} (2)(2\pi) - \left( \frac{e^{-R}}{R} \right) \left( \frac{2}{3} \right) (2\pi) \right] \\ &= \left( 1 + R + \frac{R^2}{3} \right) e^{-R} \quad (\text{AII.18}) \end{aligned}$$

### Evaluation of Integral K

### Evaluation of Integral S

### ANNEXURE III Conventional Representation of $sp^3$ Hybrid Orbitals

The four  $sp^3$  hybrid orbitals  $\psi_1, \psi_2, \psi_3$  and  $\psi_4$  may be represented by four vectors whose tips lie at the points having coordinates equal to the respective coefficients of p orbitals, that is, at  $P(\sqrt{3}/2, 0, 0)$ ,  $Q(-1/2\sqrt{3}, 0, \sqrt{2}/3)$ ,  $R(-1/2\sqrt{3}, 1/\sqrt{2}, -1/\sqrt{6})$  and  $S(-1/2\sqrt{3}, -1/2, -1/\sqrt{6})$ , respectively. Figure AIII.1 displays only the point P. The length of each vector is  $\sqrt{3}/2$  which is the square root of the sum of coefficients of  $p_x, p_y$  and  $p_z$  orbitals in each of the four hybrid orbitals.

Let the point P be rotated clockwise by an angle  $\theta = 35.27^\circ$  ( $= 180^\circ - 109.467^\circ$ ) about the y-axis followed by the anticlockwise rotation by an angle  $\phi = 45^\circ$  about the z-axis (see, Fig. AIII.1). The coordinates of the shifted point may be obtained by the following transformation expression.

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} \cos \varphi & -\sin \varphi & 0 \\ \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \cos \theta & 0 & -\sin \theta \\ 0 & 1 & 0 \\ \sin \theta & 0 & \cos \theta \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

This gives

$$X = x \cos \varphi \cos \theta - y \sin \varphi - z \cos \varphi \sin \theta$$

$$Y = x \sin \varphi \cos \theta + y \cos \varphi - z \sin \varphi \sin \theta$$

$$Z = x \sin \theta + z \cos \theta$$

The shifted location of the point P has the following coordinates.

$$X = \left(\frac{\sqrt{3}}{2}\right)\left(\frac{1}{\sqrt{2}}\right)\left(\frac{\sqrt{2}}{\sqrt{3}}\right) - 0 + 0 = \frac{1}{2}$$

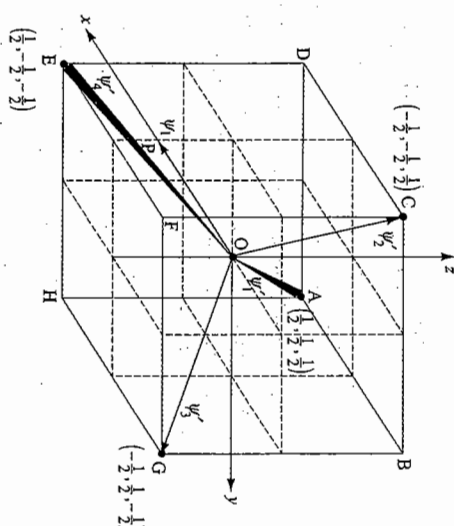
$$Y = \left(\frac{\sqrt{3}}{2}\right)\left(\frac{1}{\sqrt{2}}\right)\left(\frac{\sqrt{2}}{\sqrt{3}}\right) + 0 - 0 = \frac{1}{2}$$

$$Z = \left(\frac{\sqrt{3}}{2}\right)\left(\frac{1}{\sqrt{3}}\right) = \frac{1}{2}$$

The shifted point is located at the corner A of the cube as shown in Fig. AIII.1.

The shifted locations of the points Q, R and S are as follows.

Fig. AIII. 1  
A tetrahedron  
arrangement within a  
cube



Point Q  $(-1/2\sqrt{3}, 0, \sqrt{2}/3)$

$$X = -\frac{1}{2\sqrt{3}} \cdot \frac{1}{\sqrt{2}} \cdot \frac{\sqrt{2}}{\sqrt{3}} - 0 - \frac{\sqrt{2}}{\sqrt{3}} \cdot \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{3}} = -\frac{1}{6} - \frac{1}{6} - \frac{1}{6} = -\frac{1}{2}$$

$$Y = -\frac{1}{2\sqrt{3}} \cdot \frac{1}{\sqrt{2}} \cdot \frac{\sqrt{2}}{\sqrt{3}} - 0 - \frac{\sqrt{2}}{\sqrt{3}} \cdot \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{3}} = -\frac{1}{6} - \frac{1}{6} - \frac{1}{6} = -\frac{1}{2}$$

$$Z = -\frac{1}{2\sqrt{3}} \cdot \frac{1}{\sqrt{3}} + \frac{\sqrt{2}}{\sqrt{3}} \cdot \frac{1}{\sqrt{2}} = -\frac{1}{6} + \frac{2}{6} = \frac{1}{3}$$

The shifted location is represented by the point C of the cube shown in Fig. AIII.1.

Point R  $(-1/2\sqrt{3}, 1/\sqrt{2}, -1/\sqrt{6})$

$$X = -\frac{1}{2\sqrt{3}} \cdot \frac{1}{\sqrt{2}} \cdot \frac{\sqrt{2}}{\sqrt{3}} - \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{3}} + \frac{1}{\sqrt{6}} \cdot \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{3}} = -\frac{1}{6} - \frac{1}{6} + \frac{1}{6} = -\frac{1}{6}$$

$$Y = -\frac{1}{2\sqrt{3}} \cdot \frac{1}{\sqrt{2}} \cdot \frac{\sqrt{2}}{\sqrt{3}} + \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{3}} + \frac{1}{\sqrt{6}} \cdot \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{3}} = -\frac{1}{6} + \frac{1}{6} + \frac{1}{6} = \frac{1}{6}$$

$$Z = -\frac{1}{2\sqrt{3}} \cdot \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{6}} \cdot \frac{1}{\sqrt{2}} = -\frac{1}{6} - \frac{1}{6} = -\frac{1}{3}$$

The shifted location is represented by the point G of the cube shown in Fig. AIII.1.

Point S  $(-1/2\sqrt{3}, -1/\sqrt{2}, -1/\sqrt{6})$

$$X = -\frac{1}{2\sqrt{3}} \cdot \frac{1}{\sqrt{2}} \cdot \frac{\sqrt{2}}{\sqrt{3}} + \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{6}} \cdot \frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{3}} = -\frac{1}{6} + \frac{1}{6} - \frac{1}{6} = -\frac{1}{6}$$

$$Y = -\frac{1}{2\sqrt{3}}\frac{1}{\sqrt{2}}\sqrt{3} - \frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{6}}\frac{1}{\sqrt{2}}\sqrt{3} = -\frac{1}{6} - \frac{1}{2} + \frac{1}{6} = -\frac{1}{2}$$

$$Z = -\frac{1}{2\sqrt{3}}\frac{1}{\sqrt{3}} - \frac{1}{\sqrt{6}}\frac{1}{\sqrt{3}} = -\frac{1}{6} - \frac{1}{3} = -\frac{1}{2}$$

The shifted location is represented by the point E of the cube shown in Fig. AIII.1. The shifted vectors shown in Fig. AIII.1 are actually the conventional representations of the four  $sp^3$  hybrid orbitals, the wave functions of these orbitals are as follows.

$$\psi'_1 = \frac{1}{2}\psi_s + \frac{1}{2}\psi_{p_x} + \frac{1}{2}\psi_{p_y} + \frac{1}{2}\psi_{p_z}$$

$$\psi'_2 = \frac{1}{2}\psi_s - \frac{1}{2}\psi_{p_x} - \frac{1}{2}\psi_{p_y} + \frac{1}{2}\psi_{p_z}$$

$$\psi'_3 = \frac{1}{2}\psi_s - \frac{1}{2}\psi_{p_x} + \frac{1}{2}\psi_{p_y} - \frac{1}{2}\psi_{p_z}$$

$$\psi'_4 = \frac{1}{2}\psi_s + \frac{1}{2}\psi_{p_x} - \frac{1}{2}\psi_{p_y} - \frac{1}{2}\psi_{p_z}$$

# 3 Electrical and Magnetic Properties of Molecules

## 3.1 INTRODUCTION

This chapter deals with the structural information that can be derived when a substance is placed in an electrostatic or a magnetic field. The basic electrical property of a molecule is its dipole moment which helps understanding the relative location of various bonds in the molecule. The study of a substance in a magnetic field helps knowing whether the substance is paramagnetic or diamagnetic. Paramagnetism in a molecule is due to the presence of one or more than one unpaired electron whereas in diamagnetism, no such unpaired electron is present. Thus, this helps understanding the electronic configurations of atoms and molecules.

## 3.2 ELECTRIC DIPOLE MOMENT

### Definition of Dipole Moment

The spatial distribution of bonding electrons between the two nuclei of a diatomic molecule depends on the nature of the two involved atoms. For homonuclear diatomic molecules such as  $H_2$ ,  $N_2$ , etc., the distribution of electronic cloud is symmetrical around the two nuclei of the molecule. In heteronuclear diatomic molecules such as  $HCl$ ,  $HBr$ , etc., the charge distribution is not symmetrical, the bonding electrons are more near to the more electronegative atom. Consequently, the molecule acquires separation of charges at the two ends; the more electronegative atom serves as the negative end and the positive end is the lesser electronegative atom. The distribution of charges in a molecule can be described by a physical quantity, known as the dipole moment. It is represented by the symbol  $p$ . For diatomic molecules, the dipole moment is defined as the product of the charge  $Q$  at either end of the molecule and the distance  $r$  between the two charges (i.e. internuclear distance). Mathematically, it is defined as

$$p = Qr \quad (3.2.1)$$

The dipole moment is a vector quantity, i.e. it has both magnitude as well as direction. It can be represented by an arrow which indicates the direction from negative to positive end of the molecule. The length of the arrow is directly proportional to the magnitude of the dipole moment (Fig. 3.2.1a).

The definition of dipole moment given in Eq. (3.2.1) can be expressed as the vector additions, i.e.

$$p = \sum_i Q_i r_i \quad (3.2.2)$$

where  $Q_i$  is the charge of the  $i$ th species and  $r_i$  is the vector length of this charge from any arbitrary distance point. For example, the dipole moment of the molecule shown in Fig. 3.2.1a may be defined as shown in Fig. 3.2.1b, i.e.

$$p = (+Q)r_1 + (-Q)r_2 = Q(r_1 - r_2) = Qr \quad (3.2.3)$$

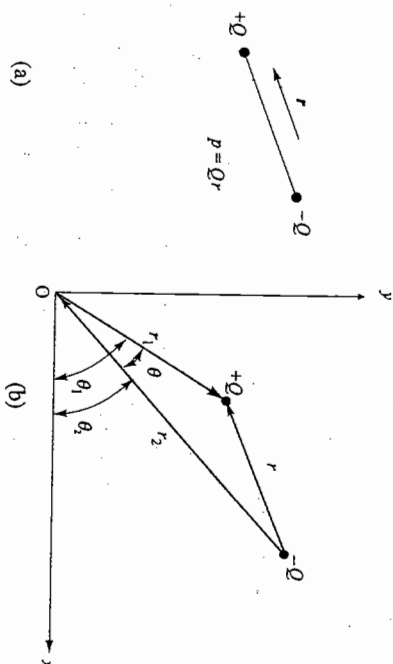


Fig. 3.2.1  
Representation of  
dipole moment

### Component Method of Adding Vectors

The vector addition shown in Fig. 3.2.1b can be conveniently carried out by making use of the expression

$$p = (p_x^2 + p_y^2)^{1/2}$$

where  $p_x$  and  $p_y$  are the  $x$ - and  $y$ -components of the dipole moment. From Fig. 3.2.1b, we have

$$p_x = (+Q)r_1 \cos \theta_1 + (-Q)r_2 \cos \theta_2$$

$$p_y = (+Q)r_1 \sin \theta_1 + (-Q)r_2 \sin \theta_2$$

Thus  $p^2 = \{(+Q)r_1 \cos \theta_1 + (-Q)r_2 \cos \theta_2\}^2$

$$+ \{(+Q)r_1 \sin \theta_1 + (-Q)r_2 \sin \theta_2\}^2$$

$$= Q^2 r_1^2 + Q^2 r_2^2 - 2Q^2 r_1 r_2 \cos \theta_1 \cos \theta_2 - 2Q^2 r_1 r_2 \sin \theta_1 \sin \theta_2$$

$$= Q^2 \{r_1^2 + r_2^2 - 2r_1 r_2 (\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2)\}$$

$$= Q^2 \{r_1^2 + r_2^2 - 2r_1 r_2 \cos(\theta_1 - \theta_2)\}$$

$$= Q^2 r^2$$

### Dipole Moment of More than Two Charges

The definition of dipole moment given by Eq. (3.2.2) may be extended to any assembly of charges. Example 3.2.1 illustrates one such case.

For polyatomic molecules, Eq. (3.2.2) may be written as

$$p = \int r \rho(r) d\tau \quad (3.2.4)$$

where  $\rho(r)$  is charge density at a position defined by the vector  $r$  and  $d\tau$  is the volume element.

### Example 3.2.1

For the assembly of charges shown in Fig. 3.2.2, evaluate the expression of the dipole moment. Given: The angle between the dashed lines is  $30^\circ$ .

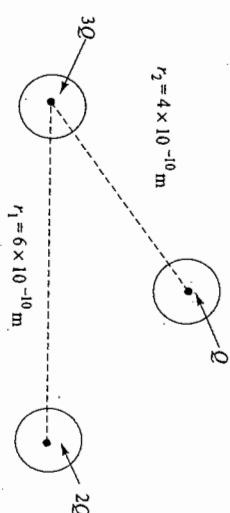


Fig. 3.2.2 The given  
assembly of charges

### Solution

Let us have the origin at  $3Q$  charge as shown in Fig. 3.2.2.

Thus, we have

$$p = \sum_i Q_i r_i = (3Q)(0) + (2Q)r_1 + (Q)r_2$$

$$= (2Q)r_1 + (Q)r_2$$

Now

$$p_x = p_x \cos \theta + p_y \sin \theta$$

$$= (2Q)(6 \times 10^{-10} \text{ m}) \cos 0^\circ + Q(4 \times 10^{-10} \text{ m}) \cos 30^\circ$$

$$= (2Q)(6 \times 10^{-10} \text{ m}) + Q(4 \times 10^{-10} \text{ m})(\sqrt{3}/2)$$

$$= Q(15.464 \times 10^{-10} \text{ m})$$

$$p_y = p_y \cos \theta + p_x \sin \theta$$

$$= (2Q)(6 \times 10^{-10} \text{ m}) \sin 0^\circ + Q(4 \times 10^{-10} \text{ m}) \sin 30^\circ$$

$$= Q(2 \times 10^{-10} \text{ m})$$

Now

$$p = (p_x^2 + p_y^2)^{1/2}$$

$$= \{Q^2 (15.464 \times 10^{-10} \text{ m})^2 + Q^2 (2 \times 10^{-10} \text{ m})^2\}^{1/2}$$

$$= Q(15.593 \times 10^{-10} \text{ m})$$

$$\tan \phi = \frac{p_y}{p_x} = \frac{Q(2 \times 10^{-10} \text{ m})}{Q(15.464 \times 10^{-10} \text{ m})} = 0.128$$

$$\phi = 7.3^\circ$$

Since  $p = (\text{charge})(\text{distance})$ , we will have

CGS-esu units The unit of  $p$  is esu cm.

SI units The unit of  $p$  is C m.

If one electronic charge is separated from an equal positive charge by a distance of 0.1 nm, its dipole moment would be

CGS-esu units

$$p = (4.8 \times 10^{-10} \text{ esu})(1.0 \times 10^{-8} \text{ cm}) = 4.8 \times 10^{-18} \text{ esu cm}$$

**SI units**

$$p = (1.602 \times 10^{-19} \text{ C}) (1.0 \times 10^{-10} \text{ m}) = 1.602 \times 10^{-29} \text{ C m}$$

Most of molecules possess dipole moment of the order of  $10^{-18}$  esu cm. In order to express the dipole moment of molecules in simpler numbers,  $10^{-18}$  esu cm unit of dipole moment is named as the *Debye unit* and is represented by the symbol D. It is obvious that

$$4.8 \text{ D} = 1.602 \times 10^{-29} \text{ C m}$$

$$\text{Hence } 1 \text{ D} = \frac{1.602 \times 10^{-29} \text{ C m}}{4.8} = 3.3356 \times 10^{-30} \text{ C m} \quad (3.2.5)$$

**Induced Dipole Moment**

The electronic distribution of a molecule is distorted in the presence of a static electric field and thus an induced dipole moment is generated. All molecules having symmetric or nonsymmetric charge distribution are polarizable in the presence of an electrostatic field and thus carry induced dipole moment. In general, the induced dipole moment in a molecule is directly proportional to the strength of the electrostatic field, i.e.

$$p_{\text{ind}} \propto E$$

$$\text{or } p_{\text{ind}} = \alpha E \quad (3.2.6)$$

where  $\alpha$  is the constant of proportionality and is a measure of easiness with which a molecule can be polarized, and is known as the *polarizability* of the molecule. By definition  $\alpha$  is equal to the induced dipole moment generated by a unit strength of an electrostatic field.

The molecule in the presence of an electrostatic field is polarized in three different ways as follows.

**Electronic polarization** In this, the electronic cloud of the molecule is distorted towards the positive end of the electrostatic field. The corresponding polarizability is represented as  $\alpha_e$ .

**Atomic polarization** In this, the nuclei (atoms) are distorted towards the negative end of the field. The corresponding polarizability is represented as  $\alpha_a$ .

**Orientation polarization** This is operative only when the molecule carries a permanent dipole moment. The electrostatic field tends to orient the molecular dipoles along the field direction. The corresponding polarizability is represented as  $\alpha_o$ .

The total polarizability  $\alpha$  of the molecule is an algebraic sum of the above three polarizabilities, i.e.

$$\alpha = \alpha_e + \alpha_a + \alpha_o \quad (3.2.7)$$

The electronic and atomic polarizations taken together is referred to as *distortion polarization*. Thus, distortion polarizability  $\alpha_d$  is given as

$$\alpha_d = \alpha_e + \alpha_a \quad (3.2.8)$$

**Unit of Polarizability**

Since  $\alpha = p_{\text{ind}}/E$ , we have

**CGS-esu units** The unit is  $\frac{\text{esu cm}}{\text{esu cm}^{-2}} = \text{cm}^3$

that is, the unit of  $\alpha$  is the unit of volume.

**SI units** Here we have

$$\frac{\text{C m}}{\text{N C}^{-1}} = \text{C}^2 \text{ m N}^{-1}$$

In the SI system,  $\alpha/4\pi\epsilon_0$  has the unit of volume as shown below.

$$\frac{\alpha}{4\pi\epsilon_0} = \frac{\text{C}^2 \text{ m N}^{-1}}{\text{C}^2 \text{ N}^{-1} \text{ m}^{-2}} = \text{m}^3$$

**3.3 EFFECT OF A DIELECTRIC ON THE ELECTROSTATIC FIELD OF A PARALLEL PLATE CAPACITOR**

Let  $\sigma$  be the charge density on the parallel plates of a capacitor. From Eq. (A.10) of Annexure at the end of this chapter, we have

$$\text{Electrostatic field } E_0 \text{ without dielectric} = \frac{\sigma}{\epsilon_0} \quad (3.3.1)$$

$$\text{Electrostatic field } E \text{ with dielectric} = \frac{\sigma}{\epsilon} \quad (3.3.2)$$

where  $\epsilon_0$  and  $\epsilon$  are the permittivities of vacuum and medium, respectively.

Since  $\epsilon$  is greater than  $\epsilon_0$  for most of dielectric, we have

$$E < E_0 \quad (3.3.3)$$

that is, the presence of a dielectric in a parallel plate capacitor decreases its electrical field. This decrease is explained as follows.

The charge density  $\sigma$  on the plates polarizes the molecules of the dielectric and thereby generates induced dipole moment in the molecules. These induced dipoles, in turn, are oriented in the field; positive ends of dipoles point towards the negatively charged plate and negative ends towards the positively charged plate as shown in Fig. 3.3.1.

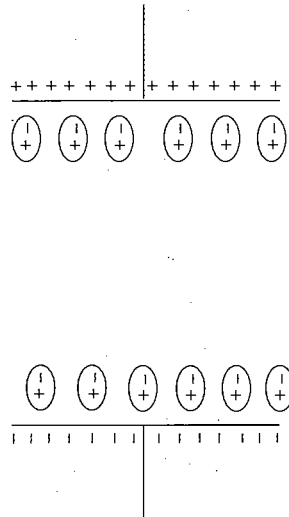


Fig. 3.3.1 Distortion and orientation of molecules in an electrostatic field

This arrangement of molecules adjacent to the plates decreases the net charge on the plates. If  $\sigma_{\text{ind}}$  is the induced charge per unit area on each plate, we will have

$$\text{Net charge per unit area on each plate} = \sigma - \sigma_{\text{ind}} \quad (3.3.4)$$

The term  $\sigma_{\text{ind}}$  is known as *polarization*. The factor  $\sigma_{\text{ind}}$  will also be equal to the induced dipole moment per unit volume of the dielectric. This may be understood as follows.

$\sigma_{\text{ind}}$  = Induced positive or negative charge per unit area of the plate

$$\text{i.e. } \sigma_{\text{ind}} = \frac{\text{Induced charge}}{\text{Unit of area}}$$

Multiplying and dividing by a unit of length, we have

$$\begin{aligned} \sigma_{\text{ind}} &= \frac{(\text{Induced charge})(\text{Unit of length})}{(\text{Unit of area})(\text{Unit of length})} \\ &= \frac{\text{Induced dipole moment}}{\text{Unit of volume}} \end{aligned}$$

Making use of Eq. (3.3.4), we may write the electrostatic field  $E$  in the presence of a dielectric as

$$E = \frac{\sigma - \sigma_{\text{ind}}}{\epsilon_0} \quad (3.3.5)$$

Substituting Eq. (3.3.1) in Eq. (3.3.5), we find that

$$E = E_0 - \frac{\sigma_{\text{ind}}}{\epsilon_0} \quad (3.3.6)$$

Dividing Eq. (3.3.6) by  $E$  and making use of Eq. (A1.11) of Annexure (i.e.  $\epsilon_r = \epsilon/\epsilon_0 = E_0/E$ , where  $\epsilon_r$  stands for relative permittivity), we get a relation which on rearranging gives

$$E = \frac{(\sigma_{\text{ind}}/\epsilon_0)}{(\epsilon/\epsilon_0) - 1} \quad (3.3.7)$$

Equation (3.3.7) relates the electrostatic field with the distortion polarization and the relative permittivity (or the dielectric constant) of the dielectric in the capacitor.

### 3.4 CLAUSIUS-MOSOTTI EQUATION

The Clausius-Mosotti equation relates the distortion polarizability of the molecule with the dielectric constant of the substance. The required relationship may be derived as follows.

Let  $N^*$  be the number of molecules per unit volume of the dielectric material and let  $P_{\text{ind}}$  be the induced dipole moment on each of the molecule. Since the polarization  $\sigma_{\text{ind}}$  represents induced dipole moment per unit volume of the dielectric, we have

$$\sigma_{\text{ind}} = N^* P_{\text{ind}} \quad (3.4.1)$$

#### Expression of Polarizability with Induced Dipole Interactions

If  $\alpha_d$  is the distortion polarizability of the molecule, we have

$$P_{\text{ind}} = \alpha_d E \quad (\text{Eq. 3.2.6})$$

Substituting  $P_{\text{ind}}$  in Eq. (3.4.1), we get

$$\sigma_{\text{ind}} = N^* \alpha_d E \quad (3.4.2)$$

If  $V_m$  is the molar volume of the dielectric, we will have

$$N^* = \frac{N_A}{V_m} = \frac{N_A}{M/\rho} = \left( \frac{N_A}{M} \right) \rho \quad (3.4.3)$$

where  $\rho$  is the density of the medium. Substituting Eqs (3.4.3) and (3.3.7) in Eq. (3.4.2), we get

$$\sigma_{\text{ind}} = \left( \frac{N_A}{M} \rho \right) (\alpha_d) \left( \frac{\sigma_{\text{ind}}/\epsilon_0}{(\epsilon/\epsilon_0) - 1} \right)$$

$$\text{or } \alpha_d = \frac{1}{N_A} (\epsilon - \epsilon_0) \left( \frac{M}{\rho} \right) \quad (3.4.4)$$

Since  $\alpha_d$  is a molecular property, it is expected to be independent of the density of the medium. Thus, from Eq. (3.4.4), it may be concluded that the quantity  $(\epsilon - \epsilon_0)/\rho$  is independent of the density of the medium. However, this is found to be so only when the molecules do not possess any permanent dipole moment and for which the pressure is low so that the interaction between neighbouring induced dipoles is negligible because of the relatively larger distance between them. Equation (3.4.4) does not hold good at high pressure and for the condensed phases because of the considerable interaction between the neighbouring induced dipoles. If this interaction is taken into account, the expression of electrical field as given by Eq. (3.3.5) modifies to

$$E_{\text{int}} = \frac{\sigma - \sigma_{\text{ind}} + \sigma_{\text{ind}}/3}{\epsilon_0} = E + \frac{\sigma_{\text{ind}}}{3\epsilon_0} \quad (3.4.5)$$

where  $\sigma_{\text{ind}}/3\epsilon_0$  is the factor which takes into account the interaction terms. Equation (3.4.2) in the present case becomes

$$\sigma_{\text{ind}} = N^* \alpha_d E_{\text{int}} \quad (3.4.6)$$

Substituting  $E_{\text{int}}$  from Eq. (3.4.6) and  $E$  from Eq. (3.3.7) in Eq. (3.4.5), we get

$$\left( \frac{\sigma_{\text{ind}}}{N^* \alpha_d} \right) = \frac{\sigma_{\text{ind}}/\epsilon_0}{(\epsilon/\epsilon_0) - 1} + \frac{\sigma_{\text{ind}}}{3\epsilon_0}$$

$$\text{or } \left( \frac{1}{N^* \alpha_d} \right) = \frac{1/\epsilon_0}{(\epsilon/\epsilon_0) - 1} + \frac{1}{3\epsilon_0} \quad (3.4.7)$$

$$\frac{(\epsilon/\epsilon_0) - 1}{(\epsilon/\epsilon_0) + 2} = \left( \frac{1}{3\epsilon_0} \right) \alpha_d N^* = \left( \frac{1}{3\epsilon_0} \right) (\alpha_d) \left( \frac{N_A}{M} \rho \right)$$

$$\text{or } \frac{(\epsilon/\epsilon_0) - 1}{(\epsilon/\epsilon_0) + 2} \frac{M}{\rho} = \frac{1}{3\epsilon_0} N_A \alpha_d \quad (3.4.8)$$



Equation (3.4.8) is known as the *Clausius-Mosottii equation*. The left side of Eq. (3.4.8) is known as *molar polarization* and is represented as  $P_m$ . From Eq. (3.4.8), it follows that  $P_m$  is independent of temperature as the right side of this equation is independent of temperature.

Clausius-Mosottii equation is found to be applicable only for nonpolar molecules which do not possess permanent dipole moment. Examples include  $H_2$ ,  $CH_4$  and  $CO_2$ . For molecules such as  $HCl$ ,  $CH_3Cl$ ,  $H_2O$ ,  $NH_3$ , etc., which have permanent dipole moment, the Clausius-Mosottii equation fails very badly. Moreover, the molar polarization of such molecules as determined from Eq. (3.4.8) varies with temperature.

### 3.5 DEBYE EQUATION

The reason why the Clausius-Mosottii equation is not applicable to polar molecules was put forward by Debye. According to him, the effect of an applied electrostatic field, besides producing distortion polarization, is to align molecular dipoles in the field direction. This polarization is known as the orientation polarization. The only factor which opposes the orientation polarization is the thermal energy of molecules. Larger the thermal energy, greater the randomness and hence lesser will be the orientation polarization. Since thermal energy of gaseous system depends on temperature, it follows that the value of orientation polarization depends on the temperature of the system.

In general, the orientation polarization depends on the following two factors.

- Directly proportional to the average value of component of permanent dipole moment  $p$  of the molecule in the applied electric field direction.
- Inversely proportional to the temperature of the system.

Detailed calculations have shown that the orientation polarization is given by

$$\alpha_o = \frac{p^2}{3kT} \quad (3.5.1)^\dagger$$

Since total polarizability is the sum of distortion and orientation polarizabilities (Eq. 3.2.7), we have

$$\alpha_{\text{total}} = \alpha_d + \alpha_o \quad (3.5.2)$$

For polar molecules, the Clausius-Mosottii equation modifies to

$$\frac{(\epsilon/\epsilon_0) - 1}{(\epsilon/\epsilon_0) + 2} \frac{M}{\rho} = \frac{1}{3\epsilon_0} N_A \alpha_{\text{total}} \quad (3.5.3)$$

Equation (3.5.3) is known as *Debye equation*. Making use of Eqs. (3.5.1) and (3.5.2), Eq. (3.5.3) becomes

$$\frac{(\epsilon/\epsilon_0) - 1}{(\epsilon/\epsilon_0) + 2} \frac{M}{\rho} = \frac{1}{3\epsilon_0} N_A (\alpha_d + \alpha_o) = \frac{1}{3\epsilon_0} N_A \left\{ \alpha_d + \frac{p^2}{3kT} \right\}$$

$$\text{that is, } P_m = \frac{1}{3\epsilon_0} N_A \left\{ \alpha_d + \frac{p^2}{3kT} \right\} \quad (3.5.4)$$

<sup>†</sup> For the derivation of Eq. (3.5.1), see Annexure II at the end of this chapter.

### Graphical Display of Debye Equation

Figure 3.5.1

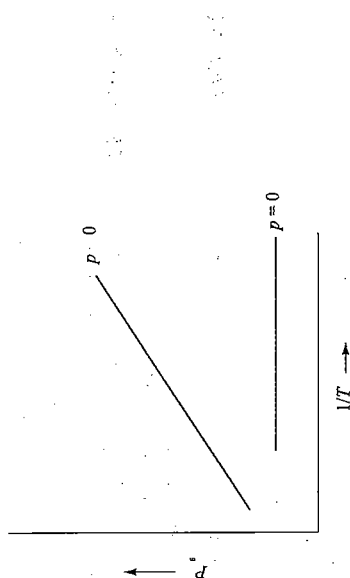


Fig. 3.5.1 Plots of  $P_m$  versus  $1/T$  for the two gaseous systems

### Example 3.5.1

For  $SO_2(g)$  at 273 K and 1 atm pressure, the dielectric constant (or relative permittivity) is 1.009 93. This molecule has a permanent dipole moment of 1.63 D. Assuming that  $SO_2$  behaves as an ideal gas, calculate per mol of (a) total, (b) orientation, (c) induced polarizations, and (d) distortion polarizability.

We have

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} = 1.009\ 93$$

$$p = 1.63\ \text{D} = 1.63\ (3.335\ 6 \times 10^{-30}\ \text{C m})$$

$$V_m = 22\ 414\ \text{cm}^3\ \text{mol}^{-1}\ \text{at 1 atm and 273 K}$$

(a) Total polarization,

$$P_{\text{total}} = \frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} = \frac{1.009\ 93 - 1}{1.009\ 93 + 2} \times 22\ 414\ \text{cm}^3\ \text{mol}^{-1} = 73.95\ \text{cm}^3\ \text{mol}^{-1}$$

(b) Orientation polarization,

$$P_o = \frac{N_A}{3\epsilon_0} \left( \frac{p^2}{3kT} \right) = \left\{ \frac{6.023 \times 10^{23}\ \text{mol}^{-1}}{3(8.854 \times 10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2})} \right\} \left\{ \frac{(1.63 \times 3.335\ 6 \times 10^{-30}\ \text{C m})^2}{3(1.38 \times 10^{-23}\ \text{J K}^{-1})(273\ \text{K})} \right\} = 59.31 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1} = 59.31\ \text{cm}^3\ \text{mol}^{-1}$$

(c) Induced polarization,

$$P_{\text{ind}} = P_{\text{total}} - P_0 = 73.95 \text{ cm}^3 \text{ mol}^{-1} - 59.31 \text{ cm}^3 \text{ mol}^{-1} \\ = 14.64 \text{ cm}^3 \text{ mol}^{-1}$$

(d) Distortion polarizability,

$$\alpha_d = \frac{P_{\text{ind}}}{N_A} = \frac{14.64 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}}{(1/3 \times 8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(6.023 \times 10^{23} \text{ mol}^{-1})} \\ = 6.46 \times 10^{-40} \text{ C}^2 \text{ N}^{-1} \text{ m}$$

At STP, the dipole moment of  $\text{NH}_3$  is reported to be 1.44 D and the atomic and electronic polarization total about  $6.0 \text{ cm}^3 \text{ mol}^{-1}$ . Calculate the dielectric constant or permittivity of  $\text{NH}_3$  at 1 atm and 273 K if  $\text{NH}_3$  is a perfect gas.

We have  $p = 1.44 \text{ D} = 1.44 (3.3356 \times 10^{-30} \text{ C m})$

$$P_d = P_e + P_a = 6.0 \text{ cm}^3 \text{ mol}^{-1}$$

$$V_m = 22414 \text{ cm}^3 \text{ mol}^{-1} \text{ at 1 atm and 273 K}$$

The Debye equation is

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} = \frac{1}{3\epsilon_0} N_A \left( \alpha_d + \frac{p^2}{3kT} \right) = \frac{1}{3\epsilon_0} N_A \alpha_d + \frac{1}{3\epsilon_0} N_A \frac{p^2}{3kT}$$

$$\text{Now } \frac{1}{3\epsilon_0} N_A \alpha_d = (6.0 \times 10^{-6}) \text{ m}^3 \text{ mol}^{-1}$$

$$\frac{N_A}{3\epsilon_0} \frac{p^2}{3kT} = \left\{ \frac{(6.023 \times 10^{23} \text{ mol}^{-1})}{(3(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}))} \right\} \left\{ \frac{(1.44 \times 3.3356 \times 10^{-30} \text{ C m})^2}{(3(1.38 \times 10^{-23} \text{ J K}^{-1})(273 \text{ K}))} \right\}$$

$$= 46.29 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} (22414 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) = (6.0 \times 10^{-6} + 46.29 \times 10^{-6}) \text{ m}^3 \text{ mol}^{-1}$$

$$= 52.29 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

$$\text{Hence } \frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{52.29 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}}{22414 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}} = 0.00233$$

Solving for  $\epsilon_r$ , we get

$$\epsilon_r = 1.007$$

Now  $\epsilon_r = \epsilon/\epsilon_0$ , therefore

$$\epsilon = \epsilon_r \epsilon_0 = (1.007) (8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}) \\ = 8.916 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$$

### 3.6. EXPERIMENTAL METHOD TO DETERMINE $\alpha$ AND $p$

#### Application for Gaseous System

For a substance in the gaseous phase,  $\alpha$  and  $p$  may be determined from the slope and intercept of linear plot of  $P_m$  versus  $1/T$  (Debye equation). We have

$$\text{Slope, } b = \frac{N_A}{3\epsilon_0} \left( \frac{p^2}{3k} \right)$$

$$\text{Hence } p = \sqrt{\frac{9\epsilon_0 k b}{N_A}} \quad (3.6.1)$$

$$\text{Intercept, } a = \text{distortion polarization} = \frac{N_A}{3\epsilon_0} \alpha_d \quad (3.6.2)$$

$$\text{Hence Distortion polarizability, } \alpha_d = \left( \frac{3\epsilon_0}{N_A} \right) a \quad (3.6.3)$$

$$\text{Orientation polarizability, } \alpha_o = \frac{p^2}{3kT} \quad (3.6.4)$$

$$\text{Orientation polarization} = \frac{b}{T} \quad (3.6.5)$$

The above method of determining  $\alpha$  and  $p$  is applicable only for gaseous systems. For condensed systems, the Debye equation cannot be applied as such because of stronger interactions among the closely packed polar molecules. The Debye equation can, however, be applied for dilute solutions of a polar substance in a nonpolar solvent. Though the polar molecules are relatively far apart, yet there exists considerable solute-solute and solute-solvent interactions. The solute-solute interactions can, in principle, be eliminated by extrapolating the plot of  $P_m$  versus  $x_2$  to zero amount fraction of solute in solution. The procedure to be adopted is now summarized.

Let the measurement of dielectric constants  $D_{12}$  (i.e. relative permittivities) and densities  $\rho_{12}$  of dilute solutions of the polar substance in a nonpolar solvent be made over a range of temperatures. At each temperature, molar polarization  $P_{12}$  of the solution is determined from the expression

$$P_{12} = \frac{D_{12} - 1}{D_{12} + 2} \frac{M_{\text{av}}}{\rho_{12}} \quad (3.6.6)$$

where

$$M_{\text{av}} = x_1 M_1 + x_2 M_2 \quad (3.6.7)$$

where  $x_1$  and  $x_2$  are amount fractions of solvent and solute, respectively. The molar polarization  $P_{12}$  of the solution includes contributions from both solute and solvent polarizations. If it be assumed that these polarizations are directly proportional to the respective amount fractions, we have

$$P_{12} = x_1 P_1 + x_2 P_2 = (1 - x_2) P_1 + x_2 P_2 \\ = P_1 + (P_2 - P_1) x_2 \quad (3.6.8)$$

The molar polarization  $P_1$  of the pure solvent can be determined from the values of dielectric constant and density of pure solvent. Knowing  $P_2$ ,  $P_1$  and  $x_2$ , the apparent molar polarization  $P_2$  of the solute can be determined from Eq. (3.6.8). The values of  $P_2$  thus obtained are found to vary with amount fraction of solute in solution. This variation is attributed to the solute-solute interactions and can be minimized by extrapolating the plot of  $P_2$  versus  $x_2$  to zero value of  $x_2$ . This gives the value of  $P_2$  at infinite dilution and is represented as  $P_{2\infty}$ . Knowing  $P_{2\infty}$  at different temperatures, the dipole moment  $p$  of the solute can be obtained by using the Debye equation. This method, however, does not eliminate the solute-solvent interactions.

### Example 3.6.1

The following data have been reported for  $\text{NH}_3(\text{g})$ .

Temperature/K	250	275	300	350
Dielectric constant	1.008 5	1.007 1	1.006 1	1.004 5
Specific volume/ $\text{cm}^3 \text{ g}^{-1}$	1 180	1 305	1 420	1 670

Calculate the dipole moment of the  $\text{NH}_3$  molecule.

Table 3.6.1 includes the given data along with the calculated values of  $P_m$ .

Table 3.6.1 Calculation of  $P_m$  from the Given Data

$T$ K	$K$ $T$	Relative permittivity, $\epsilon_r$	Molar volume $V_m/\text{cm}^3 \text{ mol}^{-1}$	Molar polarization, $P_m$ $\left( \frac{\epsilon_r - 1}{\epsilon_r + 2} \right) V_m/\text{cm}^3 \text{ mol}^{-1}$
250	0.004 00	1.008 5	1 180 $\times$ 17	56.8
275	0.003 64	1.007 1	1 305 $\times$ 17	52.5
300	0.003 33	1.006 1	1 420 $\times$ 17	49.1
350	0.002 86	1.004 5	1 670 $\times$ 17	42.6

In Fig. 3.6.1, the calculated values of  $P_m$  have been plotted against  $1/T$ . The slope of the straight-line plot is  $12\,200 \text{ cm}^3 \text{ K mol}^{-1}$ . Hence

$$\begin{aligned}
 p &= \left( \frac{9\epsilon_0 k \times \text{slope}}{N_A} \right)^{1/2} && \text{(Eq. 3.7.2b)} \\
 &= \left[ \frac{9(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(1.38 \times 10^{-23} \text{ J K}^{-1})(12\,200 \times 10^{-6} \text{ m}^3 \text{ K mol}^{-1})}{6.023 \times 10^{23} \text{ mol}^{-1}} \right]^{1/2} \\
 &= 4.72 \times 10^{-30} \text{ C m} \\
 &= (4.72 \times 10^{-30} \text{ C m}) \left( \frac{1 \text{ D}}{3.3356 \times 10^{-30} \text{ C m}} \right) = 1.415 \text{ D}
 \end{aligned}$$

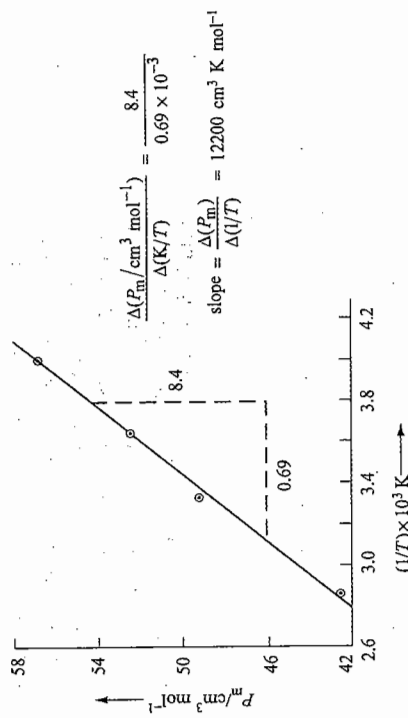


Fig. 3.6.1 The plot of  $P_m$  versus  $1/T$

### 3.7 VARIATION OF MOLAR POLARIZATION WITH THE FREQUENCY OF ELECTRIC FIELD

The molar polarization of polar molecules as described by the Debye equation is

$$P_m = \frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} = \frac{N_A}{3\epsilon_0} (\alpha_d + \alpha_o) \quad (3.7.1)$$

The value of dielectric constant is determined by placing the substance between the plates of a capacitor connected to an alternating current of frequency about 1 MHz ( $\nu = 10^6 \text{ s}^{-1}$ ). It is found that the value of relative permittivity  $\epsilon_r$  (or molar polarization  $P_m$ ) does not remain constant as the frequency of alternating electric field is increased. The variation in  $\epsilon_r$  is due to the fact that the polar molecules behave differently in the different frequency range of the alternating electric field as described in the following.

Consider a set of polar molecules in an electric field and imagine that the field is suddenly turned off. A finite time is required for the molecules to lose their partial alignment and to reach the random distribution of orientations. This time is known as the *relaxation time*. When the field is suddenly applied in the reverse direction, again a finite time is required for the orientation polarization to build up to its equilibrium value. Now imagine that the reversal of field direction occurs at an increasing frequency. As long as the frequency is not high, the molecules can follow the field and both the dielectric constant and the molar polarization remain constant. When, however, the period of alternations ( $\approx 1/\nu$ ) becomes comparable with relaxation time, this is no longer the case. The molecules cannot stay in phase with the field and the polarization drops because the contribution from the orientation polarization decreases. The frequency range at which this change occurs is usually  $10^{10} - 10^{12} \text{ Hz}$ .

At still higher frequencies, the orientation polarization completely disappears and only the distortion contribution remains. The latter results from the distortion of electrons and nuclei from their equilibrium positions. As the frequency of the alternating electric field is further increased, the nuclei can no longer follow the

alternating field because of their relatively large mass. Consequently, the molar polarization further drops. This happens when the frequency of the alternating electric field passes through the range corresponding to the infrared region of the electromagnetic spectrum to the visible region ( $\approx 10^{15}$  Hz). The only remaining polarization is due to the electronic polarization which persists even at higher frequencies. The variation of molar polarization with the frequency of the alternating field is displayed in Fig. 3.7.1.

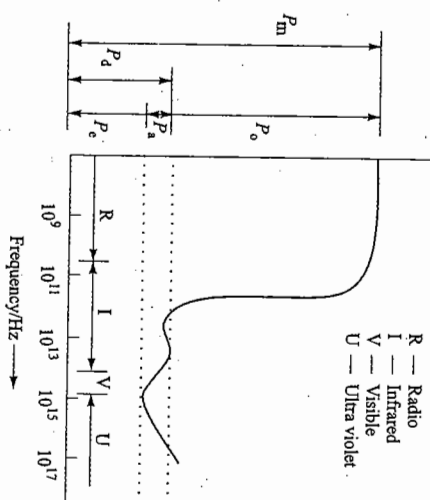


Fig. 3.7.1 Variation of  $P_m$  with frequency of the field

### 3.8 LORENTZ-LORENZ EQUATION

It was seen in the previous section that the molar polarization induces only the electronic polarization when the substance under study is subjected to alternating electric field of frequency about  $10^{15}$  Hz. Under these conditions, Eq. (3.7.1) may be written as

$$P_e = \frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} = \frac{N_A}{3\epsilon_0} \alpha_e \quad (3.8.1)$$

Equation (3.8.1) cannot be utilized as such to calculate the electronic polarization as the data of relative permittivity are measured by employing alternating current of low frequency of the order of  $10^6$  Hz. However, this difficulty is removed by employing Maxwell relation

$$\epsilon_r = n^2 \quad (3.8.2)$$

where  $n$  is the index of refraction of the dielectric. Equation (3.8.2) requires that both relative permittivity  $\epsilon_r$  and index of refraction  $n$  be measured at the same frequency. In actual practice, the relative permittivity, as stated above, is determined by electrical method using the alternating current of frequency  $\leq 10^6$  Hz while the index of refraction is measured by optical techniques at much higher frequencies ( $> 10^{14}$  Hz). For nonpolar molecules, Eq. (3.8.2) is true even though these quantities are measured at different frequencies. The reason being that the

orientation polarizability is altogether absent in such type of molecules and that the nuclei distortion polarizability has a negligible value in comparison to the electronic distortion polarizability. In other words, the measurements of  $\epsilon_r$  and  $n$  at different frequencies include only electronic polarization and hence, Eq. (3.8.2) holds good for nonpolar molecules. For polar molecules, Eq. (3.8.2) will be applicable provided both  $\epsilon_r$  and  $n$  are measured at the same frequency. Since such measurements are not feasible, Eq. (3.8.2) does not hold good for polar molecules. The dielectric constant measurement includes all three polarizabilities, viz., orientation, electronic and nuclei, whereas the index of refraction includes only the electronic polarizability. The major contribution to the total polarizability is from the orientation polarizability. Consequently, the value of relative permittivity differs very much from that of index of refraction. In support of this, we cite examples of benzene and water.

For benzene  $\epsilon_r = 2.27$  and  $n = 1.50$  : Hence  $\epsilon_r \neq n^2$   
(nonpolar)

For water  $\epsilon_r = 80$  and  $n = 1.33$  : Hence  $\epsilon_r \neq n^2$   
(polar)

Thus, electronic polarization of a molecule (polar or nonpolar) may be determined by replacing  $\epsilon_r$  by  $n^2$  in Eq. (3.8.1), such that

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} = \frac{N_A}{3\epsilon_0} \alpha_e \quad (3.8.3)$$

Equation (3.8.3) is known as *Lorentz-Lorenz equation*. The quantity

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho}$$

is known as *molar refraction* and is represented by the symbol  $R_m$ .

Both molar polarization and molar refraction are additive quantities, i.e. the molar values of these properties for a molecule can be obtained by adding the appropriate atomic values.

#### Example 3.8.1

The index of refraction of gaseous  $AB_2$  molecule at 273 K and 760 mmHg is 1.000 516 and its dielectric constant is 1.001. (a) Calculate its dipole moment. (b) How are the atoms arranged in the molecule?

Since for the given molecule, we find that  $D \approx n^2$ , the molecule  $AB_2$  is nonpolar (i.e. its dipole moment is zero). Thus, the arrangement of the atoms in  $AB_2$  is B—A—B.

#### Solution

#### Example 3.8.2

Calculate the value of molar refraction for  $CH_3Br$ , given the same for the following compounds.

$CH_3I$  19.5 cm<sup>3</sup> mol<sup>-1</sup>,  $CH_3Br$  14.5 cm<sup>3</sup> mol<sup>-1</sup>,  $HBr$  9.9 cm<sup>3</sup> mol<sup>-1</sup> and  $CH_4$  6.8 cm<sup>3</sup> mol<sup>-1</sup>.

Also calculate the values of molar refraction of C, H, Br, and I.

Since molar refraction of a molecule can be obtained by the addition of appropriate molar refractions of atoms, we have

$$R_{CH_3I} = R_C + 3R_H + R_I = 19.5 \text{ cm}^3 \text{ mol}^{-1} \quad (i)$$

$$R_{CH_3Br} = R_C + 3R_H + R_{Br} = 14.5 \text{ cm}^3 \text{ mol}^{-1} \quad (ii)$$

#### Solution

$$R_{\text{HBr}} = R_{\text{H}} + R_{\text{Br}} = 9.9 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{iii})$$

$$R_{\text{CH}_4} = R_{\text{C}} + 4R_{\text{H}} = 6.8 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{iv})$$

Adding Eqs (i) and (ii) and then subtracting Eq. (iv), we get—

$$R_{\text{C}} + 2R_{\text{H}} + R_{\text{Br}} + R_{\text{I}} = (19.5 + 14.5 - 6.8) \text{ cm}^3 \text{ mol}^{-1} = 27.2 \text{ cm}^3 \text{ mol}^{-1}$$

$$\text{Thus } R_{\text{CH}_2\text{BrI}} = 27.2 \text{ cm}^3 \text{ mol}^{-1}$$

Molar refractions of atoms can be calculated as follows.

Subtracting Eq. (iii) from Eq. (ii), we get

$$R_{\text{C}} + 2R_{\text{H}} = 4.6 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{v})$$

Subtracting Eq. (v) from Eq. (iv), we get

$$2R_{\text{H}} = 2.2 \text{ cm}^3 \text{ mol}^{-1}$$

$$\text{or } R_{\text{H}} = 1.1 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{vi})$$

From Eq. (iii), we get

$$R_{\text{Br}} = 9.9 \text{ cm}^3 \text{ mol}^{-1} - R_{\text{H}} = 9.9 \text{ cm}^3 \text{ mol}^{-1} - 1.1 \text{ cm}^3 \text{ mol}^{-1}$$

$$= 8.8 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{vii})$$

From Eq. (ii), we get

$$R_{\text{C}} = 14.5 \text{ cm}^3 \text{ mol}^{-1} - 3R_{\text{H}} - R_{\text{Br}} = (14.5 - 3.3 - 8.8) \text{ cm}^3 \text{ mol}^{-1}$$

$$= 2.4 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{viii})$$

Finally, from Eq. (i) we have

$$R_{\text{I}} = 19.5 \text{ cm}^3 \text{ mol}^{-1} - R_{\text{C}} - 3R_{\text{H}} = (19.5 - 2.4 - 3.3) \text{ cm}^3 \text{ mol}^{-1}$$

$$= 13.8 \text{ cm}^3 \text{ mol}^{-1} \quad (\text{ix})$$

### Example 3.8.3

The index of refraction of gaseous paraffin  $\text{C}_n\text{H}_{2n+2}$  is found to be 1.00139 when the gas is at STP. Given the molar refractions as 1.1 and  $2.42 \text{ cm}^3 \text{ mol}^{-1}$  for H and C, respectively, determine the formula for the hydrocarbon.

Molar refraction of the molecule,

$$R_{\text{m}} = \left( \frac{1.00139^2 - 1}{1.00139^2 + 2} \right) (22414 \text{ cm}^3) = 20.75 \text{ cm}^3 \text{ mol}^{-1}$$

This will also be given by

$$R_{\text{m}} = nR_{\text{C}} + (2n + 2)R_{\text{H}}$$

Substituting the values, we get

$$20.75 \text{ cm}^3 \text{ mol}^{-1} = n(2.42 \text{ cm}^3 \text{ mol}^{-1}) + (2n + 2)(1.1 \text{ cm}^3 \text{ mol}^{-1})$$

$$\text{or } n(2.42 \text{ cm}^3 \text{ mol}^{-1} + 2.2 \text{ cm}^3 \text{ mol}^{-1}) = 20.75 \text{ cm}^3 \text{ mol}^{-1} - 2.2 \text{ cm}^3 \text{ mol}^{-1} \\ = 18.55 \text{ cm}^3 \text{ mol}^{-1}$$

$$\text{or } n = \frac{18.55 \text{ cm}^3 \text{ mol}^{-1}}{4.62 \text{ cm}^3 \text{ mol}^{-1}} = 4.02 \approx 4$$

Hence, the compound is  $\text{C}_4\text{H}_{10}$

### 3.9 UNION OF THE DEBYE AND THE LORENTZ-LORENZ EQUATIONS

It is possible to determine the dipole moment of polar molecules by taking measurements at one temperature as compared to the Debye method where measurements at various temperatures are required. This is possible by the union of Debye and Lorentz-Lorentz equation. This can be done as follows.

$$\text{Debye equation } P_{\text{m}} = \frac{N_{\text{A}}}{3\epsilon_0} (\alpha_{\text{e}} + \alpha_{\text{a}} + \alpha_{\text{o}}) \quad (3.9.1)$$

$$\text{Lorentz-Lorentz equation } R_{\text{m}} = \frac{N_{\text{A}}}{3\epsilon_0} \alpha_{\text{e}} \quad (3.9.2)$$

From Eqs (3.9.1) and (3.9.2), we find that

$$P_{\text{m}} - R_{\text{m}} = \frac{N_{\text{A}}}{3\epsilon_0} (\alpha_{\text{a}} + \alpha_{\text{o}}) \quad (3.9.3)$$

Since  $\alpha_{\text{a}}$  is much smaller than  $\alpha_{\text{o}}$ , we may write Eq. (3.9.3) as

$$P_{\text{m}} - R_{\text{m}} \approx \frac{N_{\text{A}}}{3\epsilon_0} \alpha_{\text{o}} = \frac{N_{\text{A}}}{3\epsilon_0} \left( \frac{p^2}{3kT} \right) \quad (3.9.4)$$

$$\text{Hence } p = \left( \frac{9\epsilon_0 k}{N_{\text{A}}} \right)^{1/2} \{(P_{\text{m}} - R_{\text{m}})T\}^{1/2} \\ = \left( \frac{9(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(1.38 \times 10^{-23} \text{ J K}^{-1})}{6.023 \times 10^{23} \text{ mol}^{-1}} \right)^{1/2} \{(P_{\text{m}} - R_{\text{m}})T\}^{1/2}$$

$$\text{i.e. } p/C_{\text{m}} = (4.273 \times 10^{-29}) \{(P_{\text{m}} - R_{\text{m}})/\text{m}^3 \text{ mol}^{-1}\}^{1/2} (7/K)^{1/2} \quad (3.9.5)$$

$P_{\text{m}}$  and  $R_{\text{m}}$  appearing in Eq. (3.9.5) can be determined from the dielectric constant and index of refraction of the substance, respectively. For polar molecules in a nonpolar solvent,  $P_{2\infty}$  is used in place of  $P_{\text{m}}$ . The value of  $R_{\text{m}}$  can be calculated from the index of refraction and the density of the pure polar substance.

The value of dipole moment obtained by the use of Eq. (3.9.5) is not so reliable as those obtained by the temperature variation method owing to the uncertainty in the value of molar polarization of atoms. For a polar liquid in a nonpolar solvent,  $P_{2\infty}$  and  $R_{2\infty}$  may be employed in place of  $P_{\text{m}}$  and  $R_{\text{m}}$ , respectively, in order to get more reliable results as these values eliminate the solute-solute interactions.

### Example 3.9.1

The following data refer to dilute solutions of benzal chloride ( $\text{C}_6\text{H}_5\text{CHCl}_2$ ) in benzene at 298 K.

Amount fraction of $\text{C}_6\text{H}_5\text{CHCl}_2$	Density $\text{g cm}^{-3}$	Refractive index	Relative permittivity
0.000 00	0.874 0	1.502 00	2.272 7
0.013 14	0.880 6	1.502 94	2.353 4
0.018 43	0.883 6	1.503 37	2.386 1
0.026 04	0.888 1	1.503 87	2.433 0

Calculate the dipole moment of benzal chloride.

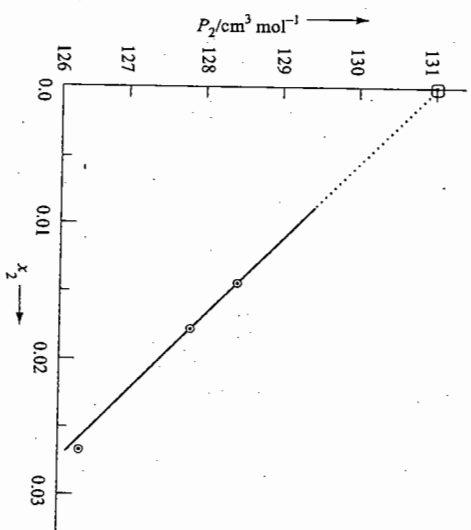
**Solution**

(i) *Evaluation of  $P_{2\infty}$*   
First of all, the values of  $P_2$  at different concentrations were calculated. From the obtained values of  $P_2$ , the molar polarization contribution  $P_2$  of the solute at different concentrations are calculated. Finally, a plot of  $P_2$  versus  $x_2$  is made. The plot was extrapolated to  $x_2 \rightarrow 0$  to obtain the value of  $P_{2\infty}$ . Table 3.9.1 includes the data of calculations.

**Table 3.9.1** Calculation of  $P_2$  at Different Values of Amount Fraction of Solute

$x_2$	$\frac{\rho}{g\ cm^{-3}}$	$\frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M_{av} (= \sum x_i M_i)}{g\ mol^{-1}}$	$P_{12} = \frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho}$ $cm^3\ mol^{-1}$	$\frac{P_{X_1}}{cm^3\ mol^{-1}}$	$P_2 = \frac{P_{12} - P_{X_1}}{x_2}$ $cm^3\ mol^{-1}$
0.0000	0.8740	0.29787	78.108	26.620	—
0.01314	0.8806	0.31086	79.196	27.959	128.54
0.01843	0.8836	0.31602	79.630	28.480	127.56
0.02604	0.8881	0.32326	80.267	29.217	126.34

Figure 3.9.1 shows the plot of  $P_2$  versus  $x_2$ . The extrapolated value of  $P_{2\infty}$  is found to be  $131.0\ cm^3\ mol^{-1}$ .

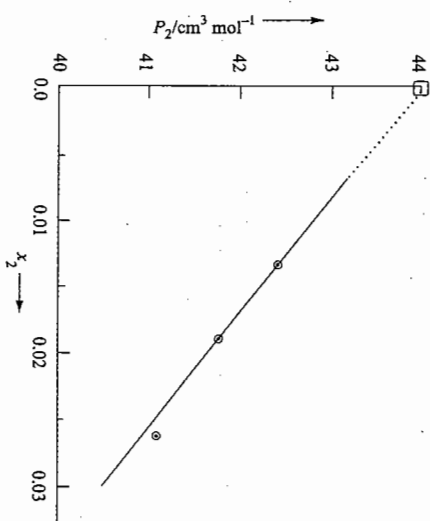
**Fig. 3.9.1** The plot of  $P_2$  versus  $x_2$ 

(ii) *Evaluation of  $R_{2\infty}$*   
In a similar way, the value of  $R_{2\infty}$  was determined. Table 3.9.2 includes the data of calculations.

**Table 3.9.2** Calculation of  $R_2$  at Different Values of Amount Fraction of Solute

$x_2$	$\frac{n^2 - 1}{n^2 + 2} \frac{M_{av}}{g\ mol^{-1}}$	$R_{12}/cm^3\ mol^{-1}$	$R_1 x_1/cm^3\ mol^{-1}$	$R_2/cm^3\ mol^{-1}$
0.0000	0.29511	78.108	26.373	—
0.01314	0.29558	79.196	26.583	42.390
0.01843	0.29579	79.630	26.657	41.780
0.02604	0.29604	80.267	26.756	41.091

Figure 3.9.2 illustrates the plot of  $R_2$  versus  $x_2$ . The value of  $R_{2\infty}$  is found to be  $44.0\ cm^3\ mol^{-1}$ .

**Fig. 3.9.2** The plot of  $R_2$  versus  $x_2$ 

Now  $P_{2\infty} = P_{o,2\infty} + P_{d,2\infty}$   
where  $P_{d,2\infty}$  and  $P_{o,2\infty}$  are molar distortion and orientation polarizations at infinite dilution, respectively.

Since atomic polarization contribution is usually less than 10%, we have

$$P_{d,2\infty} = R_{2\infty}$$

Hence  $P_{o,2\infty} = P_{2\infty} - R_{2\infty} = 131\ cm^3\ mol^{-1} - 44\ cm^3\ mol^{-1} = 87\ cm^3\ mol^{-1}$   
From  $P_{o,2\infty}$  the dipole moment  $p$  of the solute is determined as follows.

$$\text{Since } P_{o,2\infty} = \frac{N_A}{3\epsilon_0} \left( \frac{p^2}{3KT} \right)$$

$$\text{we get } p = \left\{ \left( \frac{9\epsilon_0 KT}{N_A} \right) P_{o,2\infty} \right\}^{1/2}$$

Substituting the data, we have

$$\begin{aligned}
 p &= \left\{ \left[ \frac{9(8.854 \times 10^{-12}\ C^2\ N^{-1}\ m^{-2})(1.38 \times 10^{-23}\ J\ K^{-1})(298\ K)}{6.023 \times 10^{23}\ mol^{-1}} \right] \right\}^{1/2} \\
 &\quad \times (87 \times 10^{-6}\ m^3\ mol^{-1})^{1/2} \\
 &= 6.880 \times 10^{-30}\ C\ m \\
 &= (6.880 \times 10^{-30}\ C\ m) \left( \frac{1\ D}{3.338 \times 10^{-30}\ C\ m} \right) = 2.06\ D
 \end{aligned}$$

### 3.10 IONIC CHARACTER OF DIATOMIC MOLECULES

The value of dipole moment of a diatomic molecule provides an insight into the sharing of valence electrons between the two atoms. If the electrons are equally shared, the centre of positive charge coincides with the centre of negative charge and hence the dipole moment of the molecule is zero. If the sharing is unequal the molecule has a net dipole moment. If it is assumed that the bonding electrons lie in the bond between the two atoms, the ionic character of the bond may be determined from the dipole moment of the molecule. Taking an example of HCl molecule, we find that its dipole moment is 1.03 D and its bond distance is 127.5 pm. If the two bonding electrons were completely held by chlorine, we would have a situation of 100 per cent ionic bond where chlorine and hydrogen carry uninegative and unipositive charges, respectively. Since the bond distance is 127.5 pm, the dipole moment of such a completely ionic structure (100%) would be

$$\begin{aligned} p_{\text{ionic}} &= (1.60 \times 10^{-19} \text{ C}) (127.5 \times 10^{-12} \text{ m}) \\ &= 20.4 \times 10^{-30} \text{ C m} = 6.12 \text{ D} \end{aligned}$$

On the other hand, if the bonding electrons are equally shared by H and Cl atoms, the HCl molecule would have carried zero per cent ionic character. The actual value of dipole moment is 1.03 D, suggesting that it is neither 100% ionic nor 0%, but in between. The amount of ionic character can be calculated by using the expression

$$\text{Per cent ionic character} = \frac{p_{\text{obs}}}{p_{\text{ionic}}} \times 100 \quad (3.10.1)$$

Thus, for HCl, we have

$$\text{Per cent ionic character} = \left( \frac{1.03 \text{ D}}{6.12 \text{ D}} \right) (100) \approx 17$$

### 3.11 BOND MOMENTS

It was seen in Section 3.2 that the bond connecting the two atoms of different electronegativity constitutes an electric dipole. Evidently in a poly-atomic molecule, each bond is associated with its own dipole moment value and net dipole moment of the molecule is the vector addition of these bond moments. Taking an example of water molecule, we find that it contains two bond moments inclined at an angle of 105° (Fig. 3.11.1). Let  $p_{\text{OH}}$  be the bond moment of O—H bond. From Fig. 3.11.1, it is obvious that

$$p_{\text{H}_2\text{O}} = 2 p_{\text{OH}} \cos (\theta/2) \quad (3.11.1)$$

where  $\theta = 105^\circ$ . The dipole moment of water is 1.85 D. Thus, we have

$$p_{\text{OH}} = \frac{p_{\text{H}_2\text{O}}}{2 \cos (\theta/2)} = \frac{1.85 \text{ D}}{2 \cos (52.5^\circ)} = \frac{1.85 \text{ D}}{2 \times 0.6085} = 1.52 \text{ D}$$

Note the vector addition of bond moments along the line perpendicular to the dashed line is zero.

While employing the expression of the type given by Eq. (3.11.1), it has been assumed that the contribution of nonbonding electrons (if any) towards the total dipole moment is included within the bond moments of the molecule.

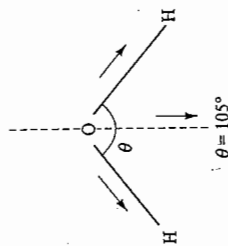
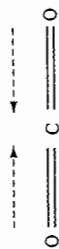


Fig. 3.11.1 Vector addition of bond moments in water molecules

If the molecule has a centre of symmetry, its dipole moment is zero. In such molecules, though the individual bonds may have bond moments, but the arrangement of the bonds is such that the resultant dipole moment is zero. For example, in carbon dioxide molecule, the two C=O bonds constitute a linear structure. Each C=O bond carries bond moment, but the vector addition of the two bond moments is zero, as shown in the following.



Methane is another example which has a zero dipole moment. Each C—H bond carries a bond moment, but the arrangement of four C—H bonds in  $\text{CH}_4$  is such that their vector addition is zero. The geometry of  $\text{CH}_4$  is tetrahedral. Obviously, the bond moment of any one C—H bond is equal and opposite to the sum of components of vectors of the rest of the three C—H bonds along the direction of the C—H bond under study, and, their sum along the line perpendicular to the C—H bond is zero.

Note that for molecules having net dipole moment equal to zero, it is not possible to derive the values of individual bond moments.

The bond moment of C—H bond, as found by Meyer, is 0.4 D with the hydrogen atom being the positive end of the dipole. With this information it is possible to evaluate the bond moment of C—X bond from the dipole moment of  $\text{CH}_3\text{X}$  molecule. Taking an example of  $\text{CH}_3\text{Cl}$  (Fig. 3.11.2), we find that vector addition of the components of three C—H bond moments along the C—Cl direction is equal to the bond moment of C—H, acting in the same direction of the Cl—C bond moment. The vector addition of components of the three C—H bond moments along the line perpendicular to the Cl—C direction is zero. Hence

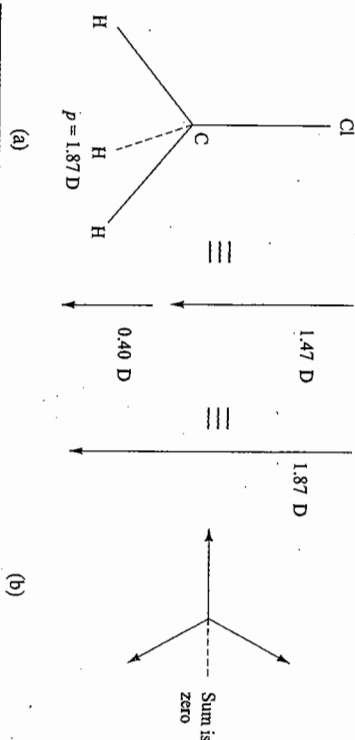
$$\begin{aligned} p(\text{CH}_3\text{Cl}) &= p(\text{Cl—C}) + p(\text{C—H}) \\ \text{or } p(\text{Cl—C}) &= p(\text{CH}_3\text{Cl}) - p(\text{C—H}) \end{aligned}$$

The experimental value of  $p(\text{CH}_3\text{Cl})$  is 1.87 D. Hence

$$p(\text{Cl—C}) = 1.87 \text{ D} - 0.4 \text{ D} = 1.47 \text{ D}$$

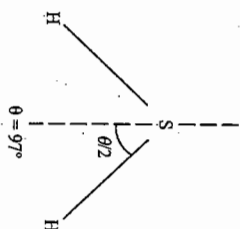


Fig. 3.11.2 Vector addition of bond moments in  $\text{CH}_3\text{Cl}$  (a) along, and (b) perpendicular to the  $\text{Cl}-\text{C}$  bond



### Example 3.11.1

The bond angle in  $\text{H}_2\text{S}$  is  $97^\circ$  and its dipole moment is  $1.47 \text{ D}$ . Find the  $\text{S}-\text{H}$  bond moment. Estimate the ionic character of the  $\text{S}-\text{H}$  bond in  $\text{H}_2\text{S}$ . The  $\text{S}-\text{H}$  bond distance is  $133.4 \text{ pm}$ .



### Solution

From the above figure, we find that

$$p = 2p_{\text{SH}} \cos(\theta/2) \quad \text{or} \quad p_{\text{SH}} = \frac{p}{2 \cos(\theta/2)}$$

Substituting the values, we get

$$p_{\text{SH}} = \frac{1.47 \text{ D}}{2 \cos(48.5^\circ)} = \frac{1.47 \text{ D}}{1.325} = 1.11 \text{ D}$$

Per cent ionic character

$$= \frac{p_{\text{SH}}}{p_{\text{ionic}}} \times 100 = \frac{1.11 \times 3.3356 \times 10^{-30} \text{ C m}}{(1.60 \times 10^{-19} \text{ C})(133.4 \times 10^{-12} \text{ m})} \times 100 \approx 17$$

Note that the sum of components of bond moments along the line perpendicular to the dashed line is zero.

### Example 3.11.2

#### Solution

Estimate the dipole moments of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  molecules. Given:  $p(\text{C}-\text{Cl}) = 1.47 \text{ D}$  with  $\text{Cl}$  as the negative end and  $p(\text{C}-\text{H}) = 0.4 \text{ D}$  with  $\text{C}$  as the negative end.

**$\text{CH}_3\text{Cl}$  Molecule** We consider the atoms  $\text{H}_a$  and  $\text{Cl}$  to lie on the plane A and the atoms  $\text{H}_b$  and  $\text{H}_c$  to lie on the plane B (which is perpendicular to the plane A) as shown in Fig. 3.11.4. We resolve each of the two bond moments in a plane along the two mutually perpendicular axes, of which  $x$  axis is common to both the planes (Fig. 3.11.3).

Fig. 3.11.3 Orientation of  $\text{CH}_3\text{Cl}$  molecule

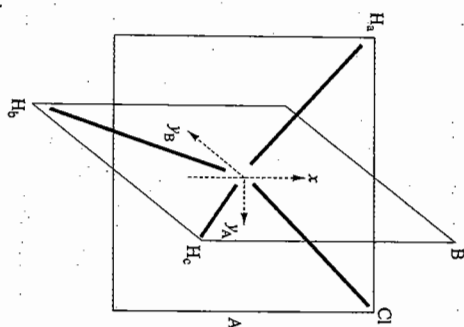


Fig. 3.11.4 Orientation of  $\text{CH}_2\text{Cl}_2$  molecule

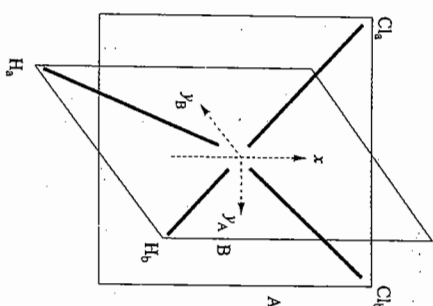


Fig. 3.11.3 Orientation of  $\text{CH}_3\text{Cl}$  molecule

Components along  $x$ -axis

$$p_x = (p_{\text{CH}_3} - p_{\text{Cl}} - p_{\text{CH}_b} - p_{\text{CH}_c}) \cos(109.48^\circ/2) = (-p_{\text{Cl}} - p_{\text{CH}}) \cos(54.74^\circ) = -(1.47 \text{ D} + 0.4 \text{ D})(0.577) = -1.08 \text{ D}$$

Components along  $y_A$

$$p_{y_A} = (-p_{\text{Cl}} - p_{\text{CH}_c}) \sin(54.74^\circ) = -(1.47 \text{ D} + 0.4 \text{ D})(0.817) = -1.53 \text{ D}$$

Components along  $y_B$

$$p_{y_B} = (p_{\text{CH}_b} - p_{\text{CH}_c}) \sin(54.74^\circ) = 0$$

The dipole moment of  $\text{CH}_3\text{Cl}$  will be

$$p = \sqrt{p_x^2 + p_{y_A}^2 + p_{y_B}^2} = \sqrt{(-1.08 \text{ D})^2 + (-1.53 \text{ D})^2 + 0^2} = 1.87 \text{ D}$$

**$\text{CH}_2\text{Cl}_2$  Molecule** We consider the atoms  $\text{Cl}_a$  and  $\text{Cl}_b$  to lie on the plane A and the atoms  $\text{H}_a$  and  $\text{H}_b$  to lie on the plane B (which is perpendicular to the plane A) as shown in Fig. 3.11.4. We resolve each of the two bond moments in a plane along the two mutually perpendicular axes, of which  $x$  axis is common to both the planes (Fig. 3.11.4).



Components along  $x$ -axis

$$\begin{aligned} p_x &= (-p_{\text{CCl}_a} - p_{\text{CCl}_b} - p_{\text{CH}_a} - p_{\text{CH}_b}) \cos (54.74^\circ) \\ &= (-1.47 \text{ D} - 1.47 \text{ D} - 0.4 \text{ D} - 0.4 \text{ D})(0.577) \\ &= -2.16 \text{ D} \end{aligned}$$

$$p_{y_A} = (+p_{\text{CCl}_a} - p_{\text{CCl}_b}) \sin (54.74^\circ) = 0$$

$$p_{y_B} = (p_{\text{CH}_a} - p_{\text{CH}_b}) \sin (54.74^\circ) = 0$$

Hence, the dipole moment of  $\text{CH}_2\text{Cl}_2$  is 2.16 D.

**$\text{CHCl}_3$  Molecule** We consider the atoms  $\text{Cl}_a$  and  $\text{Cl}_b$  to lie on the plane A and the atoms  $\text{Cl}_c$  and H on the plane B (which is perpendicular to the plane A) as shown in Fig. 3.11.5. We resolve each of the two bond moments in a plane along the two mutually perpendicular axes, of which  $x$ -axis is common to both the planes (Fig. 3.11.5)

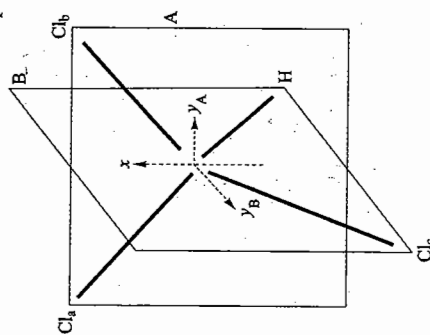


Fig. 3.11.5 Orientation of  $\text{CHCl}_3$  molecule

Components along  $x$ -axis

$$\begin{aligned} p_x &= (-p_{\text{CCl}_a} - p_{\text{CCl}_b} + p_{\text{CCl}_c} - p_{\text{CH}}) \cos (54.74^\circ) \\ &= (-p_{\text{CCl}_a} - p_{\text{CH}}) \cos (54.74^\circ) = (-1.47 \text{ D} - 0.4 \text{ D}) (0.577) \\ &= -1.08 \text{ D} \end{aligned}$$

$$p_{y_A} = (+p_{\text{CCl}_a} - p_{\text{CCl}_b}) \sin (54.74^\circ) = 0$$

$$\begin{aligned} p_{y_B} &= (-p_{\text{CCl}_c} - p_{\text{CH}}) \sin (54.74^\circ) = (-1.47 \text{ D} - 0.40 \text{ D}) (0.817) \\ &= -1.53 \text{ D} \end{aligned}$$

The dipole moment of  $\text{CHCl}_3$  will be

$$p = \sqrt{p_x^2 + p_{y_B}^2} = \sqrt{(-1.08 \text{ D})^2 + (-1.53 \text{ D})^2} = 1.87 \text{ D}$$

### Alternative Procedure

Alternatively, we may proceed as follows.  
 **$\text{CH}_3\text{Cl}$  Molecule** Let the bond moments be resolved into the Cartesian  $x$ -,  $y$ - and  $z$ -axes as shown in Fig. 3.11.6.

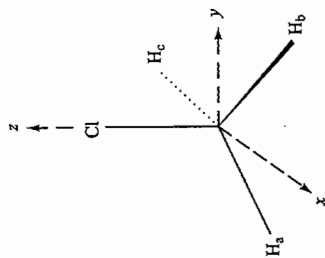


Fig. 3.11.6 Orientation of  $\text{CH}_3\text{Cl}$  molecule

We have

$$\begin{aligned} p_z &= -p_{\text{CCl}} - (p_{\text{CH}_a} + p_{\text{CH}_b} + p_{\text{CH}_c}) \cos (180^\circ - 109.48^\circ) \\ &= -1.47 \text{ D} - (0.40 \text{ D} + 0.40 \text{ D} + 0.4 \text{ D}) \cos (70.52^\circ) \\ &= -1.47 \text{ D} - (1.20 \text{ D}) (0.333) \\ &= -1.47 \text{ D} - 0.40 \text{ D} = -1.87 \text{ D} \\ p_y &= -p_{\text{CH}_a} \cos (109.48^\circ - 90^\circ) + (p_{\text{CH}_b} + p_{\text{CH}_c}) \sin (180^\circ - 109.48^\circ) \cos 60^\circ \\ &= -(0.40 \text{ D}) \cos (19.48^\circ) + 2 p_{\text{CH}} \sin (70.52^\circ) \cos 60^\circ \\ &= -(0.40 \text{ D}) (0.943) + (2 \times 0.40 \text{ D}) (0.943) (0.5) \\ &= -0.377 \text{ D} + 0.3777 \text{ D} = 0 \\ p_x &= (p_{\text{CH}_b} - p_{\text{CH}_c}) \sin (180^\circ - 109.48^\circ) \sin 60^\circ \\ &= 0 \end{aligned}$$

The dipole moment of  $\text{CH}_3\text{Cl}$  will be

$$p^2 = \sqrt{p_x^2 + p_y^2 + p_z^2} = 1.87 \text{ D}$$

**$\text{CH}_2\text{Cl}_2$  Molecule** Let the bond moments be resolved into the cartesian  $x$ -,  $y$ - and  $z$ -axes as shown in Fig. 3.11.7.

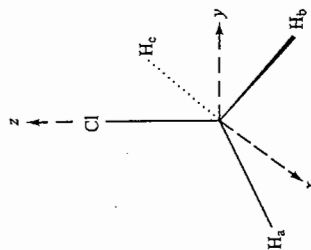


Fig. 3.11.7 Orientation of  $\text{CH}_2\text{Cl}_2$  molecule

We have

$$P_z = -P_{\text{CCl}_a} + (P_{\text{CCl}_b} - P_{\text{CH}_a} - P_{\text{CH}_b}) \cos(70.52^\circ)$$

$$= -1.47 \text{ D} + (1.47 \text{ D} - 0.40 \text{ D} - 0.40 \text{ D}) (0.333)$$

$$= -1.47 \text{ D} + 0.22 \text{ D}$$

$$= -1.25 \text{ D}$$

$$P_y = P_{\text{CCl}_b} \cos(19.48^\circ) + (P_{\text{CH}_a} + P_{\text{CH}_b}) \sin(70.52^\circ) \cos 60^\circ$$

$$= (1.47 \text{ D}) (0.943) + (0.40 \text{ D} + 0.40 \text{ D}) (0.943) (0.5)$$

$$= 1.39 \text{ D} + 0.38 \text{ D} = 1.76 \text{ D}$$

$$P_x = (P_{\text{CH}_a} - P_{\text{CH}_b}) \sin(70.52^\circ) \sin 60^\circ$$

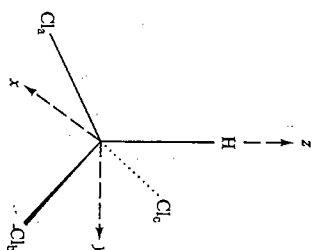
$$= 0$$

The dipole moment of  $\text{CH}_2\text{Cl}_2$  will be

$$P = \sqrt{P_x^2 + P_y^2 + P_z^2} = \sqrt{(-1.25 \text{ D})^2 + (1.76 \text{ D})^2 + 0}$$

$$= 2.16 \text{ D}$$

**CHCl<sub>3</sub> Molecule** Let the bond moments be resolved into the Cartesian  $x$ ,  $y$ - and  $z$ -axes as shown in Fig. 3.11.8.



We have

$$P_x = P_{\text{CH}} + (P_{\text{CCl}_a} + P_{\text{CCl}_b} + P_{\text{CCl}_c}) \cos(70.52^\circ)$$

$$= 0.40 + (3 \times 1.47 \text{ D}) (0.333)$$

$$= 1.87 \text{ D}$$

$$P_y = P_{\text{CCl}_a} \cos(19.48^\circ) - (P_{\text{CCl}_b} + P_{\text{CCl}_c}) \sin(70.52^\circ) \cos 60^\circ$$

$$= (1.47 \text{ D}) (0.943) - (2 \times 1.47 \text{ D}) (0.943) (0.5)$$

$$= 0$$

$$P_z = (-P_{\text{CCl}_b} + P_{\text{CCl}_c}) \sin(70.52^\circ) \sin 60^\circ$$

$$= 0$$

The dipole moment of  $\text{CHCl}_3$  molecule is

$$P = \sqrt{P_x^2 + P_y^2 + P_z^2} = 1.87 \text{ D}$$

### 3.12. GROUP MOMENTS

In evaluating the dipole moment of benzene derivatives, the study of group moment is of greater importance than the concept of bond moment. For example, in chlorobenzene, if it is assumed that all C—H linkages in benzene have zero bond moments, then the observed dipole moment of 1.55 D of chlorobenzene may be assumed to arise from the C—Cl linkage. Thus, the group moment of chlorine atom is  $-1.55 \text{ D}$ . The sign of group moment indicates the direction in which the group moment acts; positive sign implies that the group moment acts away from the benzene ring whereas negative sign implies that it acts towards the ring. Table 3.12.1 includes the group moments of a few groups.

Table 3.12.1 Group Moments of a Few Groups

Group	$\text{NO}_2$	$\text{CN}$	$\text{OH}$	$\text{Cl}$	$\text{H}$	$\text{CH}_3$	$\text{NH}_2$
Group moment/ Debye	-3.98	-3.8	-1.6	-1.58	0	+0.4	+1.53

The dipole moment of any substituted benzene can be derived from the following expression of vector addition of group moments. Consider, for example, the arrangement of two bond moments  $P_1$  and  $P_2$  inclined at an angle  $\theta$  with respect to each other. The addition of these two may be carried out by adding separately the two  $x$ - and  $y$ -components of  $P_1$  and  $P_2$  so as to give  $P_x$  and  $P_y$ , respectively, and then by employing the expression

$$P = (P_x^2 + P_y^2)^{1/2}$$

we get the resultant moment of the two moments. If  $\theta_1$  and  $\theta_2$  are the respective angles of  $P_1$  and  $P_2$  with  $x$ -axis, we have

$$P_x = P_{1,x} + P_{2,x} = P_1 \cos \theta_1 + P_2 \cos \theta_2$$

$$P_y = P_{1,y} + P_{2,y} = P_1 \sin \theta_1 + P_2 \sin \theta_2$$

Hence  $P = \{(P_1 \cos \theta_1 + P_2 \cos \theta_2)^2 + (P_1 \sin \theta_1 + P_2 \sin \theta_2)^2\}^{1/2}$

$$= \{P_1^2 + P_2^2 + 2P_1 P_2 (\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2)\}^{1/2}$$

$$P = \{P_1^2 + P_2^2 + 2P_1 P_2 \cos(\theta_1 - \theta_2)\}^{1/2}$$

$$\text{or } P = (P_1^2 + P_2^2 + 2P_1 P_2 \cos \theta)^{1/2} \quad (3.12.1)$$

Show that the dipole moment of 1,2-disubstituted benzene ( $\text{C}_6\text{H}_4\text{X}_2$ ) and 1,3-disubstituted benzene ( $\text{C}_6\text{H}_4\text{X}_2$ ) are  $1.732p$  and  $p$ , respectively, where  $p$  is the dipole moment of monosubstituted benzene ( $\text{C}_6\text{H}_5\text{X}$ ).

For 1,2-disubstituted benzene, the angle  $\theta$  between the two vectors is  $60^\circ$ . Substituting this value in the expression

$$P_{\text{total}} = (P_1^2 + P_2^2 + 2P_1 P_2 \cos \theta)^{1/2}$$

we get

$$P_{\text{total}} = (p^2 + p^2 + 2pp \cos 60^\circ)^{1/2} = \sqrt{3} p = 1.732p$$

For 1,3-disubstituted benzene, the angle  $\theta$  between the two vectors is  $120^\circ$ . Substituting this value of angle, we get

$$p_{\text{total}} = (p^2 + p^2 + 2pp \cos 120^\circ)^{1/2} = (p^2 + p^2 - 2pp \sin 30^\circ)^{1/2} = p$$

### Example 3.12.2

The dipole moment of chlorobenzene is 1.70 D. Calculate the corresponding values for 1,2- and 1,3-dichlorosubstituted benzenes. Compare these values with the experimental values of 2.53 D and 1.68 D, respectively.

From Example 3.12.1, we have

$$p_{1,2-} = 1.732 p_{\text{mono}}$$

$$p_{1,3-} = p_{\text{mono}}$$

Substituting the value of  $p_{\text{mono}}$ , we have

$$p_{1,2-} = 1.732 \times 1.70 \text{ D} = 2.94 \text{ D}$$

$$p_{1,3-} = 1.70 \text{ D}$$

Comparing these with the experimental values, we find that the agreement is excellent for 1,3-dichlorobenzene whereas for 1,2-dichlorobenzene, the agreement is not satisfactory. This may be due to either or both of the following reasons.

- The angle between C—Cl bond vectors may be larger than  $60^\circ$  because of mutual repulsion of the relatively negative chlorine atoms.
- The magnitude of bond moments may be modified by their proximity.

### Example 3.12.3

The dipole moments of nitrobenzene, toluene and chlorobenzene are 3.93 D, 0.46 D, and 1.55 D, respectively. Calculate the dipole moments of the following compounds.

- o*-, *m*-, *p*-dinitrobenzenes
- o*-, *m*-, *p*-dimethylbenzenes
- o*-, *m*-, *p*-dichlorobenzenes
- o*-, *m*-, *p*-nitrotoluenes
- o*-, *m*-, *p*-chlorotoluenes
- 1,3- and 1,4-chloronitrobenzenes

From Example 3.12.1, we have

$$p_{\text{ortho}} = \sqrt{3}p$$

$$p_{\text{meta}} = p$$

Hence, we have

- o*-, *m*-, *p*-dinitrobenzenes

$$\textit{o-dinitrobenzene} : p = 1.732 \times 3.93 \text{ D} = 6.81 \text{ D}$$

$$\textit{m-dinitrobenzene} : p = 3.93 \text{ D}$$

$$\textit{p-dinitrobenzene} : p = 0$$

- o*-, *m*-, *p*-dimethylbenzenes

$$\textit{o-dimethylbenzene} : p = 1.732 \times 0.46 \text{ D} = 0.797 \text{ D}$$

$$\textit{m-dimethylbenzene} : p = 0.46 \text{ D}$$

$$\textit{p-dimethylbenzene} : p = 0$$

- o*-, *m*-, *p*-dichlorobenzenes

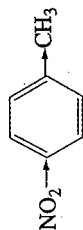
$$\textit{o-dichlorobenzene} : p = 1.732 \times 1.55 \text{ D} = 2.68 \text{ D}$$

$$\textit{m-dichlorobenzene} : p = 1.55 \text{ D}$$

$$\textit{p-dichlorobenzene} : p = 0$$

- o*-, *m*-, *p*-nitrotoluenes

We have



$$p_{\text{NO}_2} = -3.93 \text{ D} \text{ and } p_{\text{CH}_3} = 0.46 \text{ D}$$

*o*-nitrotoluene: Angle  $\theta$  is  $60^\circ$ . Hence

$$p/D = (p_1^2 + p_2^2 + 2p_1p_2 \cos \theta)^{1/2} \\ = \{(-3.93)^2 + (0.46)^2 + 2(-3.93)(0.46) \cos 60^\circ\}^{1/2} \\ = (15.445 + 0.212 - 1.808)^{1/2} = 3.72$$

*m*-nitrotoluene: Angle  $\theta$  is  $120^\circ$ . Thus

$$p/D = \{(-3.93)^2 + (0.46)^2 + 2(-3.93)(0.46) \cos 120^\circ\}^{1/2} \\ = (15.445 + 0.212 + 1.808)^{1/2} = (17.465)^{1/2} \\ = 4.18$$

*p*-nitrotoluene: Angle  $\theta$  is  $180^\circ$ . Thus

$$p/D = \{(-3.93)^2 + (0.46)^2 + 2(-3.93)(0.46) \cos 180^\circ\}^{1/2} \\ = (15.445 + 0.212 + 3.616)^{1/2} = 4.39$$

Alternatively, for *p*-nitrotoluene, the dipole moment may be derived directly by simple algebraic addition of the two dipole moments as the two vectors point in the same direction.

$$\text{Hence } p = |p_{\text{NO}_2}| + p_{\text{CH}_3} = 3.93 \text{ D} + 0.46 \text{ D} = 4.39 \text{ D}$$

- o*-, *m*-, *p*-chlorotoluenes

$$\text{Here } p_{\text{Cl}} = -1.55 \text{ D and } p_{\text{CH}_3} = 0.46 \text{ D}$$

Hence,

$$\textit{o-chlorotoluene} : p/D = \{(-1.55)^2 + (0.46)^2 + 2(-1.55)(0.46) \cos 60^\circ\}^{1/2} \\ = (2.402 + 0.212 - 0.713)^{1/2} \\ = (1.901)^{1/2} = 1.379$$

$$\textit{m-chlorotoluene} : p/D = \{(-1.55)^2 + (0.46)^2 + 2(-1.55)(0.46) \cos 120^\circ\}^{1/2} \\ = (2.402 + 0.212 + 0.713)^{1/2} \\ = (3.327)^{1/2} = 1.824$$

$$\textit{p-chlorotoluene} : p = 0.46 \text{ D} + 1.55 \text{ D} = 2.01 \text{ D}$$

- 1,3 and 1,4-chloronitrobenzenes

$$p_{\text{Cl}} = -1.55 \text{ D and } p_{\text{NO}_2} = -3.93 \text{ D}$$

1,3-chloronitrobenzene

$$p/D = \{(-3.93)^2 + (-1.55)^2 + 2(-3.93)(-1.55) \cos 120^\circ\}^{1/2} \\ = (15.445 + 2.402 - 6.092)^{1/2} \\ = 3.43$$

**1,4-chloronitrobenzene**

The two vectors point in the opposite directions, and hence the magnitude of dipole moment is

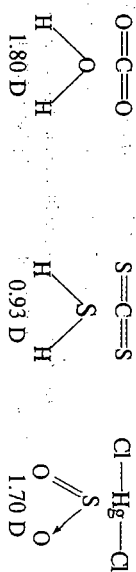
$$p = 3.93 \text{ D} - 1.55 \text{ D} = 2.38 \text{ D}$$

**3.13 APPLICATIONS OF DIPOLE MOMENTS**

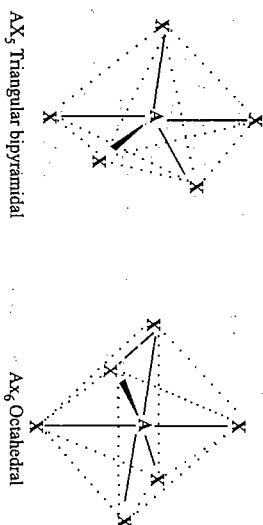
The main application of dipole moment values is in the field of molecular structure. For example, if a molecule has a centre of symmetry, its dipole moment is zero. In general, if the various identical groups are symmetrically placed around the centre of symmetry, the molecule has a zero dipole moment. A few examples illustrating the structural application of dipole moment values are now described.

**Shapes of Molecules**

The dipole measurements have been used to determine the shapes of simple molecules. For example, the triatomic molecules like  $\text{BeCl}_2$ ,  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{HgCl}_2$ , etc., have zero dipole moment whereas molecules like  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , etc., have non-zero dipole moments. Thus, it may be concluded that the former molecules are linear molecules with centre of symmetry, and the latter are nonlinear molecules. Hence, the structures are



Compounds of the type  $\text{AX}_4$  ( $\text{CH}_4$ ,  $\text{TiCl}_4$ ,  $\text{CCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{Ni(CO)}_4$ , etc.) have been found to possess zero moment. Thus, their structures are either tetrahedral or square planar. Some of  $\text{AX}_5$  ( $\text{PF}_5$ ,  $\text{PCl}_5$ ,  $\text{Fe(CO)}_5$ , etc.) and  $\text{AX}_6$  ( $\text{SF}_6$ ,  $\text{WF}_6$ ) molecules have zero moments. Thus, these molecules also have symmetrical structures. Their structures are

**Geometrical Isomers**

It is possible to distinguish between the *cis*- and *trans*-forms of a molecule from its dipole moment value. The former has a definite moment whereas the latter has zero dipole moment.

**p-Substituted Benzene Molecules**

Dipole moment values have been used to show whether the linkages  $\text{C}-\text{X}$  in *p*-substituted benzenes are coplanar with the benzene ring or not. 1,4-dichlorobenzene has zero dipole moment whereas 1,4-dihydroxybenzene

(hydroquinone) has a dipole moment of 1.64 D. It leads to the conclusion that  $\text{C}-\text{Cl}$  bonds are coplanar whereas  $\text{C}-\text{OH}$  bonds might not be so.

**3.14 MAGNETIC FIELD IN A SUBSTANCE**

In vacuum the magnetic flux density  $B$  is related to the magnetic field intensity  $H$  by the relation

$$B = \mu_0 H \quad (\text{Eq. AI.31b of Annexure I})$$

Within a substance  $B$  is, in general, not given by the above relation. It may be greater or less than  $\mu_0 H$  and is given by

$$B = \mu_0 (H + M) \quad (3.14.1)$$

where  $M$  is the magnetic moment per unit volume and is known as the *magnetization*. It is a measure of the capacity of a substance to develop magnetization when placed in a magnetic field. In SI units, it has the unit of  $\text{A m}^{-1}$ .

The magnetization of a substance is directly proportional to the applied field and is thus given by

$$M = \chi_B (B/\mu_0) \quad (3.14.2)$$

where  $\chi_B$  is the dimensionless quantity known as the *magnetic susceptibility*.

The following types of substances are of interest depending upon the sign of magnetic susceptibility.

**Paramagnetic substance** For such a substance,  $\chi_B$  is positive and has a value of the order of  $+10^{-4}$ . The magnetization of the substance has a positive value and thus  $B > H$ .

**Diamagnetic substance** For such a substance,  $\chi_B$  is negative and has a value of the order of  $-10^{-6}$ . The magnetization of the substance is negative and thus  $B < H$ .

Experimentally, the more useful quantity is the product of magnetic susceptibility and molar volume defined as

$$\begin{aligned} \chi_m &= (\text{Molar volume}) (\text{magnetic susceptibility}) \\ &= \left( \frac{M}{\rho} \right) \chi_B \quad (3.14.3) \end{aligned}$$

Since  $\chi_B$  has no unit, the unit of  $\chi_m$  is that of molar volume, i.e.  $\text{m}^3 \text{mol}^{-1}$ .

**3.15 MOLECULAR INTERPRETATION OF DIAMAGNETISM AND PARAMAGNETISM**

In the previous section, we have defined two types of magnetic materials based on the sign of intensity of magnetization. In this section, we describe the molecular interpretations of diamagnetism and paramagnetism.

The diamagnetism in atoms, ions or molecules is due to the orbital motion of electrons. A simple interpretation of diamagnetism is obtained if we imagine the motion of electrons in orbital to constitute a current flowing in a coil of wire. According to Lenz's law, when such a coil of wire is placed in a magnetic field, the field induces the current so as to produce an induced magnetic field acting in

the opposite direction of the applied magnetic field. Thus, when a substance is placed in a magnetic field, orbital motion of electrons are polarized and thus an induced magnetic field acting in the opposite direction of the external magnetic field is produced.

In case of an electric current in a wire, the induced field quickly dies out owing to the atomic resistance. Inside the atom, there is no resistance to the electronic current and thus induced magnetic field persists as long as the external magnetic field is maintained.

Diamagnetism is exhibited by all types of substances, whether the substance is diamagnetic or paramagnetic. If the substance is paramagnetic, the underlying diamagnetism is entirely concealed by the large value of magnetic moment of the substance.

Since the orbital motion of electrons is independent of the thermal energy, it follows that diamagnetism is independent of temperature of substance. Besides this, the substance has the same value of magnetic susceptibility whether it is present in the gaseous or liquid state.

If  $\alpha_m$  is the induced diamagnetic susceptibility per atom (or magnetizability), the magnetic susceptibility per mole of the substance is given by

$$\chi_m = N_A \alpha_m \quad (3.15.1)$$

As in the electrical case,  $\alpha_m$  describes the tendency of the applied field to induce an opposing field in an otherwise homogeneous medium.

P. Pascal observed that the diamagnetic susceptibilities are approximately additive and thus the diamagnetic susceptibility of a substance can be obtained by adding the appropriate atomic and bond contributions. Table 3.15.1 includes the molar diamagnetic susceptibilities for some of the atoms and bonds.

**Table 3.15.1 Molar Diamagnetic Susceptibilities for a Few Atoms and Bonds**

Atom or bond	Diamagnetic susceptibility $\times 10^{-12} \text{ m}^3 \text{ mol}^{-1}$	Atom or bond	Diamagnetic susceptibility $\times 10^{-12} \text{ m}^3 \text{ mol}^{-1}$
H	-2.93	Cl	-20.1
C	-6.00	Br	-30.6
O (in alcohols and ethers)	-4.61	C=C bond	5.5
O (in ketones)	+1.73	C=N bond	8.2
O in C=O	-3.36		
N (in open chain)	-5.57	N=N bond	1.9
N (in ring)	-4.61	C≡C bond	0.8
N (in amines)	-1.54	C=C-C=C bond	10.6
F	-11.5	Benzene ring	-1.4

## Paramagnetism

The phenomenon of paramagnetism is due to the presence of unpaired electron(s) in the atom or molecule. In Sections 1.9 and 1.10, we have seen that the orbital motion of an electron and the spinning of electron around its own axis produces tiny magnets. An external magnetic field tends to align these microscopic magnets parallel to itself, and thus produces a net positive magnetization on the microscopic level. The magnetic moments of tiny magnets are given by

$$\text{Orbital motion} \quad \mu_m = \mu_B \sqrt{l(l+1)} \quad (3.15.2)$$

$$\text{Spinning of electron} \quad \mu_m = 2 \mu_B \sqrt{s(s+1)} \quad (3.15.3)$$

where  $l$  and  $s$  are the azimuthal and spin quantum numbers, respectively, and  $\mu_B$  is the basic unit of magnetic moment called the *Bohr magneton* and is given by the expression

$$\mu_B = \frac{eh}{4\pi m_e} \quad (3.15.4)$$

Its value is

$$\begin{aligned} \mu_B &= \frac{(1.602 \times 10^{-19} \text{ C})(6.626 \times 10^{-34} \text{ J s})}{4(3.14)(9.1 \times 10^{-31} \text{ kg})} \\ &= 9.274 \times 10^{-24} \text{ J T}^{-1} \end{aligned}$$

$$(3.15.5)$$

If an atom has more than one unpaired electron, the magnetic moment due to the spins of electrons is given by

$$\mu_m = (2\mu_B) \sqrt{S(S+1)} \quad (3.15.6)$$

where  $S$  is given as

$$S = n \left( \frac{1}{2} \right) \quad (3.15.7)$$

where  $n$  is the number of unpaired electrons.

In case of molecules, the only contribution which is important is due to the spinning of electrons. The orbital contribution is found to be ineffective because the electrons are strongly held into the nuclear configuration of the molecule and thus are unable to line up with the external magnetic field. The same is also true for ions in solution. Here the interaction of orbitals of ions with the solvating molecules is apparently sufficient to prevent the orbitals being oriented in the presence of a magnetic field. Thus, the orbital contribution towards the magnetic susceptibility is generally quite small and the majority of contribution comes from the spinning of unpaired electrons.

It may be emphasized here that the paramagnetic susceptibility is entirely due to the unpaired electrons. If all the electrons are paired, the value of  $S$  is zero and thus  $\mu_m$  is also zero. This is due to the fact that the magnetic moment generated by the spinning of one electron in one direction (say,  $\alpha$ -spin) is completely balanced by the opposite spinning electron (i.e.  $\beta$ -spin). In other words, the generated dipoles have opposite polarities and are placed adjacent to each other. Thus, their effects are mutually cancelled.

The paramagnetic susceptibility contribution towards the molar magnetic susceptibility can be worked out and is found to be given by

$$\chi_m = N_A \left( \frac{\mu_0 \mu_m^2}{3kT} \right) \quad (3.15.8)$$

The value of  $\chi_m$  varies inversely with temperature. This is to be expected since the only factor which opposes the perfect alignment of dipoles is the thermal energy. Larger the thermal energy (i.e. larger temperature), lesser the alignment.

### 3.16 TOTAL MOLAR MAGNETIC SUSCEPTIBILITY

The total molar magnetic susceptibility is the algebraic sum of molar diamagnetic susceptibility and molar paramagnetic susceptibility, i.e. sum of Eqs (3.15.1) and (3.15.8). Thus, we have

$$\chi_m = N_A \left( \alpha_m + \frac{\mu_0 \mu_m^2}{3kT} \right)$$

For diamagnetic substances,  $\mu_m = 0$  and hence

$$\chi_m = N_A \alpha_m \quad (\text{Eq. 3.15.1})$$

Thus, diamagnetic susceptibility is independent of temperature.

For paramagnetic substances, both the contributions are present. For such a substance,  $\chi_m$  is usually of the order of  $10^{-3}$ – $10^{-4}$  per gram and thus the small diamagnetic contribution ( $10^{-6}$  per gram) is overwhelmed. Thus, we may write

$$\chi_m = N_A \left( \frac{\mu_0 \mu_m^2}{3kT} \right) \quad (\text{Eq. 3.15.8})$$

### 3.17 CALCULATION OF THE NUMBER OF UNPAIRED ELECTRONS

The number of unpaired electrons in an atom, molecule or ion can be worked out by combining Eqs (3.15.6) and (3.15.8). Thus, we have

$$\begin{aligned} \chi_m &= \frac{N_A \mu_0}{3kT} \mu_m^2 = \frac{N_A \mu_0}{3kT} \left\{ 2\mu_B \sqrt{S(S+1)} \right\}^2 \\ &= \frac{4\mu_B^2 \mu_0 N_A}{3kT} S(S+1) \\ &= \left[ \frac{4(9.274 \times 10^{-24} \text{ J T}^{-1})^2 (4\pi \times 10^{-7} \text{ N C}^{-2} \text{ s}^2)(6.023 \times 10^{23} \text{ mol}^{-1})}{3(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} \right] S(S+1) \\ &= 4\pi(1.68 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}) S(S+1) \quad (3.17.1) \end{aligned}$$

The molar magnetic susceptibility  $\chi_m$  can be determined experimentally. Knowing  $\chi_m$ , the value of  $S$  can be obtained from Eq. (3.17.1). The value of  $S$  thus obtained can be interpreted in terms of the number of unpaired electrons by using Eq. (3.15.7).

Table 3.17.1 shows the results to be expected for  $\chi_m$  at 298 K for various number of unpaired electrons.

Table 3.17.1 The Values of Molar Magnetic Susceptibility at 298 K

Number of unpaired electrons	Total electron spin quantum number, $S$	Spin magnetic moment, $\mu_m/\mu_B$ $= 2\sqrt{S(S+1)}$	Molar magnetic susceptibility $\chi_m/\text{m}^3 \text{ mol}^{-1}$
1	1/2	1.732	$15.84 \times 10^{-9}$
2	2/2	2.828	$42.12 \times 10^{-9}$
3	3/2	3.873	$79.09 \times 10^{-9}$
4	4/2	4.899	$126.61 \times 10^{-9}$
5	5/2	5.916	$184.53 \times 10^{-9}$
6	6/2	6.928	$252.90 \times 10^{-9}$

### 3.18 GOUY BALANCE METHOD TO MEASURE MAGNETIC SUSCEPTIBILITY

In the Gouy balance method, the sample whose magnetic susceptibility is required, is taken in a tube. The tube is suspended from one arm of a balance in such a way that it is partly in the magnetic field of an electromagnet (Fig. 3.18.1). When the magnet is turned on the following two alternatives are observed.

1. If the sample is paramagnetic, it is attracted towards the magnetic field. This attraction is due to the alignment of the tiny magnets generated in the magnetic field. The potential energy of the system is lowered because of these alignments.
2. If the sample is diamagnetic, it is repelled by the field. The system has lower potential energy outside the magnetic field.

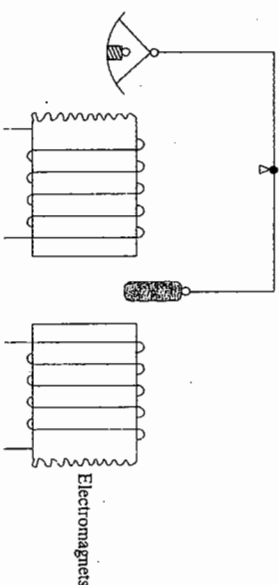


Fig. 3.18.1 Experimental set up of the Gouy balance method

Since the sample moves in a nonhomogeneous field (maximum at the centre and minimum outside the magnetic field), one has to find out the total force experienced by the sample by considering the force experienced by the small segment of the sample and then integrating the resultant expression from  $B = 0$  to

$B = B_{\max}$ . This force is related to the magnetic susceptibility and can be worked out as follows.

From Eq. (3.14.2), we have

$$M = \chi_B \left( \frac{B}{\mu_0} \right)$$

Since  $M$  represents the magnetic moment per unit volume, we may write Magnetic moment per unit volume of the sample

$$= \chi_B \left( \frac{B}{\mu_0} \right) \quad (3.18.1)$$

Consider a small segment of the length  $dz$  of the tube (Fig. 3.18.1). Let  $A$  be area of cross-section of the tube. We have

Magnetic moment of the material within the volume  $A \, dz$

$$= \chi_B \left( \frac{B}{\mu_0} \right) A \, dz \quad (3.18.2)$$

The magnetic moment acts in the direction of magnetic field. If the magnetic induction changes by a value of  $dB$  over the length  $dz$ , the change in potential energy of the sample is given by

$$\begin{aligned} dV &= -(\text{Magnetic moment}) (\text{change in magnetic induction}) \\ &= - \left\{ \chi_B \left( \frac{B}{\mu_0} \right) (A \, dz) \right\} dB \end{aligned} \quad (3.18.3)$$

The force experienced by the sample is the rate of change of potential energy with respect to  $z$ , i.e.

$$dF = - \frac{dV}{dz}$$

Thus, we have

$$dF = \chi_B A \frac{dB}{\mu_0} \quad (3.18.4)$$

The total force experienced by the sample when it moves from outside the magnetic field (where it has a zero value) to the centre of the field (where it has a maximum value) can be obtained by integration of Eq. (3.18.4). Thus, we have

$$\begin{aligned} F &= \int_0^{B=B_{\max}} dF = \int_0^{B=B_{\max}} \chi_B A \frac{dB}{\mu_0} \\ &= \frac{1}{2} \chi_B A \frac{B_{\max}^2}{\mu_0} \end{aligned} \quad (3.18.5)$$

If the buoyancy correction is included, Eq. (3.18.5) becomes

$$F = \frac{1}{2} (\chi_B - \chi_B^0) A \frac{B_{\max}^2}{\mu_0} \quad (3.18.6)$$

where  $\chi_B^0$  is the susceptibility of air.

The force  $F$  is measured in terms of the masses that are added or removed from the balance pan in order to keep the position of the sample unshifted. Thus

$$F = (\Delta m)g$$

Thus, knowing  $F$ , the magnetic susceptibility can be calculated by using Eq. (3.18.5). In practice, however, one frequently compares the force of a standard sample with that of a known sample instead of evaluating the cross-section of the tube and the magnetic field directly.

### Example 3.18.1

The ion  $\text{Co}(\text{NH}_3)_6^{3+}$  has been shown from magnetic measurements to have no unpaired electrons, whereas  $\text{CoF}_6^{3-}$  has four unpaired electrons. Considering only the effect of unpaired electrons, calculate the change in apparent mass of a  $0.1 \text{ mol dm}^{-3}$  solution of salts of these ions in 1-cm diameter test tube suspended in a Gouy balance when a magnetic field of 5 000 gauss is turned on.

For  $\text{Co}(\text{NH}_3)_6^{3+}$ ,  $\Delta m = 0$  since it contains no unpaired electron. For  $\text{CoF}_6^{3-}$ , we have

$$\chi_m = 4\pi(10.08 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}) \text{ for four unpaired electrons}$$

$$V_m = 1 \text{ dm}^3/0.1 \text{ mol} = 10^{-2} \text{ m}^3 \text{ mol}^{-1}$$

$$\mu_0 = 4\pi \times 10^{-7} \text{ N C}^{-2} \text{ s}^2$$

$$g = 9.8067 \text{ m s}^{-2}$$

$$A = \pi r^2 = 3.14 \times 0.005^2 \text{ m}^2$$

$$B = 5000 \text{ G} = 0.5 \text{ T} = 0.5 \text{ N C}^{-1} \text{ m}^{-1} \text{ s}$$

$$\text{Hence } \Delta m = \frac{1}{2g} \left( \frac{\chi_m}{V_m} \right) (A) \left( \frac{B^2}{\mu_0} \right)$$

$$= \left\{ \frac{1}{2(9.8067 \text{ m s}^{-2})} \right\} \left\{ \frac{4\pi(10.08 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1})}{10^{-2} \text{ m}^3 \text{ mol}^{-1}} \right\} (3.14 \times 0.005^2 \text{ m}^2)$$

$$\times \left\{ \frac{(0.5 \text{ N C}^{-1} \text{ m}^{-1} \text{ s})^2}{4\pi \times 10^{-7} \text{ N C}^{-2} \text{ s}^2} \right\}$$

$$= 1.01 \times 10^{-5} \text{ kg}$$

### Example 3.18.2

A sample of an organometallic compound was placed in a susceptibility balance. The following data were obtained.

$$F = 2.47 \times 10^{-4} \text{ N}; \quad A = 1.8 \times 10^{-5} \text{ m}^2, \quad B = 4000 \text{ G}$$

Find the susceptibility of the compound.

We have

$$F = 2.47 \times 10^{-4} \text{ N}$$

$$A = 1.8 \times 10^{-5} \text{ m}^2$$

$$B = 4000 \text{ G} = 0.4 \text{ T} = 0.4 \text{ N C}^{-1} \text{ m}^{-1} \text{ s}$$

Rearranging the expression

$$F = \frac{1}{2} \chi_B A \left( \frac{B^2}{\mu_0} \right)$$

for  $\kappa_B$ , we get

$$\kappa_B = \frac{2F\mu_0}{AB^2}$$

which on substituting the data gives

$$\begin{aligned}\kappa_B &= \frac{2(2.47 \times 10^{-4} \text{ N})(4\pi \times 10^{-7} \text{ N C}^{-2} \text{ s}^2)}{(1.8 \times 10^{-5} \text{ m}^2)(0.4 \text{ N C}^{-1} \text{ m}^{-1} \text{ s})^2} \\ &= 2.156 \times 10^{-4}\end{aligned}$$

### REVISIONARY PROBLEMS

3.1 Define the following terms:

- (i) Coulomb's law. (ii) Dielectric constant. (iii) Permittivity of the space. (iv) Intensity of an electrical field. (v) Electrical potential. (vi) Capacitance of a parallel plate capacitor. (vii) Induced dipole moment. (viii) Polarization of the molecule in the presence of an electrostatic field. (ix) Electronic, atomic, distortion and orientation polarizabilities.

(Hint: See Annexure I at the end of the chapter.)

3.2 Deduce the following:

- (i) 1 esu (or stat coulomb) = 1 dyn<sup>1/2</sup> cm = 1 g<sup>1/2</sup> cm<sup>3/2</sup> s<sup>-1</sup>  
 (ii) 1 C = 1 A s  
 (iii)  $D = \epsilon/\epsilon_0$   
 (iv) 1 C = 2.997 9 × 10<sup>9</sup> stat C  
 (v) The unit of volt is erg (esu)<sup>-1</sup> or J C<sup>-1</sup>  
 (vi) 1 V = 1 kg m<sup>2</sup> s<sup>-2</sup> C<sup>-1</sup>  
 (vii) 1 stat V = 1 g<sup>1/2</sup> cm<sup>-1/2</sup> s<sup>-1</sup>  
 (viii) 1 unit of  $E$  = dyn (esu)<sup>-1</sup> = 1 erg cm<sup>-1</sup> esu<sup>-1</sup> = 1 (stat V) cm<sup>-1</sup> or 1 unit of  $E$  = 1 N C<sup>-1</sup> = 1 N J<sup>-1</sup> V = 1 V m<sup>-1</sup>  
 (ix) 1 stat V = 300 V  
 (x) The unit of dipole moment is esu cm or C m  
 (xi) 1 D = 3.338 × 10<sup>-30</sup> C m  
 (xii) The unit of polarizability is cm<sup>3</sup> or C<sup>2</sup> m N<sup>-1</sup>  
 (xiii) The unit of  $\alpha/4\pi\epsilon_0$  is m<sup>3</sup>  
 (Hint: See Annexure I at the end of this chapter.)

3.3 Derive the Clausius-Mosotti equation:

$$\frac{(\epsilon/\epsilon_0) - 1}{(\epsilon/\epsilon_0) + 2} \frac{M}{\rho} = \frac{1}{3\epsilon_0} N_A \alpha_d$$

Explain, why the above equation is applicable for nonpolar molecules and not for polar molecules.

3.4 (a) Debye equation is

$$P_m = \frac{(\epsilon/\epsilon_0) - 1}{(\epsilon/\epsilon_0) + 2} \frac{M}{\rho} = \frac{1}{3\epsilon_0} N_A \left( \alpha_d + \frac{p^2}{3kT} \right)$$

Explain, the nature of plots of  $P_m$  versus  $1/T$  for (i) polar molecules and (ii) nonpolar molecules.

(b) Debye equation can be used to determine the dipole moment for molecules in gaseous system, whereas it cannot be used as such for molecules in condensed system. Explain.

(c) To determine dipole moment of molecules in condensed system, it is preferable to plot  $P_{2\infty}$  versus  $1/T$ , where  $P_{2\infty}$  is the molar polarization of solute at infinite dilution.

(d) The molar polarization of a polar molecule varies with temperature whereas that of a nonpolar molecule is independent of temperature. Explain, why it is so.

3.5 Explain, how the molar polarization varies with the frequency of an electrostatic field.

3.6 Under what conditions, does the Maxwell relation  $D = \epsilon^2$  hold good? Explain why for polar molecules  $D \neq \epsilon^2$ .

3.7 What is molar refraction? Show that it is given by

$$R_m = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} = \frac{N_A}{3\epsilon_0} \alpha_e$$

3.8 Derive the relation

$$\rho/C \text{ m} = 4.273 \times 10^{-29} \{ (P_m - R_m)/\text{m}^3 \text{ mol}^{-1} \}^{1/2} (T/K)^{1/2}$$

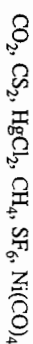
3.9 Explain, how the dipole moment of a diatomic molecule determines its per cent ionic character.

3.10 What do you understand by the terms bond moments and group moments? How does the dipole moment of a diatomic molecule or bond moment determine its per cent ionic character?

3.11 Show that the vector addition of two moments  $P_1$  and  $P_2$  inclined at an angle  $\theta$  is given by the relation

$$P^2 = P_1^2 + P_2^2 + 2P_1P_2 \cos \theta$$

3.12 The dipole moment of the following molecules is zero. What do you conclude about their geometry?



3.13 (a) The magnetic force on a moving charged particle is known as the Lorentz force and is given by

$$F = QvB$$

Show that the unit of magnetic induction  $B$  is given by

$$1 \text{ T} = 1 \text{ kg s}^{-1} \text{ C}^{-1}$$

(b) Show that  $1 \text{ T} = 10^4 \text{ G}$

(c) Show that 1 oersted = 1 A m<sup>-1</sup>/4π × 10<sup>-3</sup>

(Hint: See Annexure I.)

3.14 (a) The magnetic field at a distance  $d$  produced by an electric current  $I$  flowing in a long straight wire is

$$B = \left( \frac{\mu_0}{2\pi} \right) \frac{I}{d}$$

Show that  $\mu_0$ , the permeability of vacuum, has the unit of N C<sup>-2</sup> s<sup>2</sup>.



- (b) Making use of the expression of  $B$  given in Part (a) show that the force between two electric currents in two parallel rectilinear conductor of length  $l$  separated by a distance  $d$  in vacuum is given by

$$F = \left( \frac{\mu_0}{2\pi} \right) \frac{I_1 I_2}{d}$$

- (c) Define the basic unit of current in SI unit from the expression of  $F$  given in Part (b).

- (d) Show that  $\mu_0 = 4\pi \times 10^{-7} \text{ T m A}^{-1}$

- (e) Show that product of  $\epsilon_0$  and  $\mu_0$  is equal to  $1/c^2$ .

- 3.15 What is the difference between the magnetic field strength  $H$  and magnetic induction  $B$ ? How are they related to each other? What are the units of  $H$  in Gaussian and SI systems?

- 3.16 How is the magnetic flux density  $B$  affected in a substance? Show that the magnetic susceptibility is unitless.

- 3.17 Define paramagnetic and diamagnetic substances on the basis of their values of magnetic susceptibility and intensity of magnetization.

(Hint: See Annexure I.)

- 3.18 Show that the value of Bohr magneton is given by  $9.2741 \times 10^{-24} \text{ J T}^{-1}$ .

- 3.19 How are paramagnetism and diamagnetism explained from the molecular point of view?

- 3.20 The paramagnetic susceptibility contribution towards the molar magnetic susceptibility is given by

$$\chi_m = N_A \left( \frac{\mu_0 \mu_m^2}{3kT} \right)$$

How does the above relation help in computing the number of unpaired electrons in a molecule of a substance?

### NUMERICAL PROBLEMS

- 3.1 The index of refraction of gaseous paraffin  $C_nH_{2n+2}$  was found to be 1.38 and its density is  $0.66 \text{ g cm}^{-3}$ . Given are the molar refractions of H and C as 1.1 and  $2.42 \text{ cm}^3 \text{ mol}^{-1}$ , respectively. Calculate the molecular formula of the compound. [Ans.  $C_5H_{12}$ ]

- 3.2 Given the following data

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \quad R_m = 20.6 \text{ cm}^3 \text{ mol}^{-1}$$

$$\text{CH}_3\text{CH}_2\text{OH} \quad R_m = 12.9 \text{ cm}^3 \text{ mol}^{-1}$$

$$\text{CH}_3\text{OH} \quad R_m = 8.3 \text{ cm}^3 \text{ mol}^{-1}$$

Calculate  $R_m$  for  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ . [Ans.  $22.1 \text{ cm}^3 \text{ mol}^{-1}$ ]

- 3.3 Given the molar refractions:  $\text{CH}_4 = 6.82 \text{ cm}^3 \text{ mol}^{-1}$ ;  $\text{C}_2\text{H}_6 = 11.44 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\text{C}_3\text{H}_8 = 16.06 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} = 17.58 \text{ cm}^3 \text{ mol}^{-1}$ , calculate the molar refraction of glycol,  $\text{HOCH}_2\text{CH}_2\text{OH}$  and its index of refraction. The density of glycol is  $1.115 \text{ g cm}^{-3}$ . [Ans.  $14.48 \text{ cm}^3 \text{ mol}^{-1}$ , 1.43]

- 3.4 Calculate the dipole moment of water in the vapour state and estimate the dipole moment of each OH bond if the angle between these bonds is  $105^\circ$ . The values of the molar polarization  $P$  with temperature are tabulated below.

$T/K$	384.3	420.1	444.7	484.1	522.0
$P/\text{cm}^3 \text{ mol}^{-1}$	57.4	53.6	50.7	46.8	43.4

[Ans.  $P_{H_2O} = 1.85 \text{ D}$ ,  $p_{OH} = 1.52 \text{ D}$ ]

- 3.5 The dipole moment of  $\text{SO}_2$  is  $1.61 \text{ D}$ , the length of each S—O bond is  $0.145 \text{ nm}$  and the bonds have approximately 25% ionic character. Calculate the bond angle in  $\text{SO}_2$  molecule. [Ans.  $\theta = 124.88^\circ$ ]

- 3.6 The molar refraction for oxygen in an ether group (ROR) is  $1.643 \text{ cm}^3 \text{ mol}^{-1}$ . It is  $6.818 \text{ cm}^3 \text{ mol}^{-1}$  for methane and  $13.279 \text{ cm}^3 \text{ mol}^{-1}$  for dimethyl ether. Calculate the value for diethyl ether. [Ans.  $22.915 \text{ cm}^3 \text{ mol}^{-1}$ ]

- 3.7 A liquid of molar mass  $112.0 \text{ g mol}^{-1}$  has a refractive index 1.347, dielectric constant 4.285 and density  $1.108 \text{ g cm}^{-3}$  at  $25^\circ\text{C}$ . What are the values of its molar refraction and molar polarization? [Ans.  $21.6 \text{ cm}^3 \text{ mol}^{-1}$ ,  $52.85 \text{ cm}^3 \text{ mol}^{-1}$ ]

- 3.8 The density of ethyl alcohol at  $20^\circ\text{C}$  is  $0.789 \text{ g cm}^{-3}$  while that of methyl alcohol is  $0.792 \text{ g cm}^{-3}$ . Assuming ideal behaviour, calculate the index of refraction of a solution containing 50% by mass of each component.

Given are the molar refraction contributions: C;  $2.418 \text{ cm}^3 \text{ mol}^{-1}$ ; H;  $1.100 \text{ cm}^3 \text{ mol}^{-1}$ ; O in OH group;  $1.525 \text{ cm}^3 \text{ mol}^{-1}$ . [Ans. 1.349]

- 3.9 The molar polarization of a certain vapour is found to obey the equation

$$P/\text{cm}^3 \text{ mol}^{-1} = 60 + 20.5 K/T$$

Assuming ideal behaviour, calculate (i) molar polarization, (ii) dipole moment, (iii) index of refraction, and (iv) dielectric constant of the vapour at STP.

[Ans.  $60.08 \text{ cm}^3 \text{ mol}^{-1}$ ,  $0.058 \text{ D}$ ,  $1.004$ ,  $1.008$ ]

- 3.10 Calculate the dipole moment of diethyl ether from the following data for its solution in cyclohexane at  $20^\circ\text{C}$ .

$\chi_2$	0.123	25	0.088	54	0.047	2	0.000	0
$\epsilon_r$	2.246		2.178		2.109		2.033	
$\rho/\text{g cm}^{-3}$	0.769	1	0.772	0	0.775	1	0.778	4

The index of refraction and density of pure diethyl ether are 1.352 and  $0.710 \text{ g cm}^{-3}$ , respectively.

- 3.11 Calculate the dipole moment and the distortion polarizability of  $\text{BrF}_3$  from the following data for the dielectric constant of the vapour. Assume ideal behaviour for the calculation of molar volume. Given:  $V_m = 22.414 \text{ cm}^3 \text{ mol}^{-1}$  at  $273.15 \text{ K}$  and 1 atm.

$T/K$	345.6	374.9	402.4	430.8
$\epsilon_r$	1.006 32	1.005 52	1.004 91	1.004 38

[Hint:  $V_m(273 \text{ K}, 1 \text{ atm}) = 22.414 \text{ cm}^3 \text{ mol}^{-1}$ , calculate  $V_m(T, 1 \text{ atm}) = (22.414 \text{ cm}^3 \text{ mol}^{-1}) \times (T/273 \text{ K})$ .]

- 3.12 The magnetic susceptibility  $\chi$  for a sample at  $275 \text{ K}$  is found to be  $4.26 \times 10^{-4}$ . If the magnetic moment is  $1.91 \times 10^{-23} \text{ m}^2 \text{ A}$ , the molar mass is  $2.055 \text{ kg mol}^{-1}$ , and the density is  $0.971 \text{ kg dm}^{-3}$ , estimate the value of magnetic susceptibility,  $\chi_m$ .

- 3.13 A 0.1 mol dm<sup>-3</sup> solution of an iron coordination compound was placed in a tube of area of cross-section 1 cm<sup>2</sup> and suspended in a Gouy balance at 25°C. A magnetic field of 0.5 tesla was turned on. The net change in apparent mass after allowing for the solvent was 18.4 mg. The diamagnetic correction for the compound itself was  $-2.5 \times 10^{-9}$  m<sup>3</sup>. Calculate the number of unpaired electrons per Fe atom. Assume complete orbital moment quenching. [Ans. 5 electrons]
- (Hint: Evaluate  $\chi_g$  using Eq. (3.18.6), add  $\chi_{\text{dia}}$  and then consult Table 3.17.1.)
- 3.14 Calculate  $\chi_m$  for benzene and benzoic acid by adding the appropriate atomic and bond diamagnetic susceptibilities, and compare with the observed values of  $-54.8 \times 10^{-12}$  m<sup>3</sup> mol<sup>-1</sup> and  $-70.3 \times 10^{-12}$  m<sup>3</sup> mol<sup>-1</sup>, respectively.
- 3.15 A 0.01027 mol dm<sup>-3</sup> solution of KMnO<sub>4</sub> had an apparent mass of 9.8059 g in a magnetic field and 9.8064 g out of the field, when placed in the Gouy balance. Calculate the number of unpaired electrons for Mn(VII). [Ans.  $n = 0$ ]
- 3.16 Explain qualitatively the following facts.
- (a) At very high temperatures  $P_m(\text{HCl}) > P_m(\text{HBr}) > P_m(\text{HI})$   
 (b) At low temperatures  $P_m(\text{HCl}) < P_m(\text{HBr}) < P_m(\text{HI})$   
 (Hint: At higher temperatures, dipole contribution is not significant.)
- 3.17 The permittivity of gaseous sulphur dioxide at 1 atm as a function of temperature are as follows.
- | T/K   | 267.6  | 297.2  | 336.9  | 443.8  |
|---|--------|--------|--------|--------|
| $10^{12} \epsilon / \text{C}^2 \text{N}^{-1} \text{m}^{-2}$ | 8.9420 | 8.9261 | 8.9027 | 8.8825 |
- Estimate the dipole moment of SO<sub>2</sub>. Assume ideal behaviour. Given:  $\epsilon_0 = 8.8542 \times 10^{-12} \text{C}^2 \text{N}^{-1} \text{m}^{-2}$ . [Ans. 1.91 D]
- 3.18 The permittivity of gaseous water at 1 atm as a function of temperature are as follows.
- | T/K   | 384.3  | 420.1  | 444.7  | 484.1  | 522.0  |
|---|--------|--------|--------|--------|--------|
| $10^{12} \epsilon / \text{C}^2 \text{N}^{-1} \text{m}^{-2}$ | 8.9025 | 8.8954 | 8.8907 | 8.8855 | 8.8810 |
- Estimate the dipole moment of H<sub>2</sub>O. Assume ideal behaviour. Given:  $\epsilon_0 = 8.8542 \times 10^{-12} \text{C}^2 \text{N}^{-1} \text{m}^{-2}$ . [Ans. 1.96 D]
- 3.19 The permittivity of gaseous BrF<sub>3</sub> at 1 atm as a function of temperature are as follows.
- | T/K   | 345.6  | 374.9  | 402.4  | 430.8  |
|---|--------|--------|--------|--------|
| $10^{12} \epsilon / \text{C}^2 \text{N}^{-1} \text{m}^{-2}$ | 8.9102 | 8.9031 | 8.8977 | 8.8930 |
- Estimate the dipole moment of BrF<sub>3</sub>. Assume ideal behaviour. Given:  $\epsilon_0 = 8.8542 \times 10^{-12} \text{C}^2 \text{N}^{-1} \text{m}^{-2}$ . [Ans. 1.50 D]

## ANNEXURE I Electrostatic and Magnetic Fields

### A FEW DEFINITIONS REGARDING THE ELECTROSTATIC FIELD

A few definitions in both the units, viz., gaussian (CGS-esu) and SI, needed for the study of a substance in an electrostatic field are described below.

In CGS-esu units, the force of attraction or repulsion between two electrostatic point charges  $Q_1$  and  $Q_2$  placed at a distance  $r$  is defined as

$$F = \frac{Q_1 Q_2}{D r^2} \quad (\text{A1.1})$$

where  $D$  is the dielectric constant of the medium. For air or more precisely for a vacuum,  $D = 1$ . If  $Q_1$  and  $Q_2$  have the same sign (+ve and +ve or -ve and -ve),  $F$  is a positive quantity meaning that the force between the two charges is repulsive; if  $Q_1$  and  $Q_2$  have opposite signs,  $F$  is a negative quantity implying that the force is attractive.

In CGS-esu system, Eq. (A1.1) is taken as the basis for defining a unit of electrostatic charge (esu). The two unit charges (known as stat coulomb, stat C) placed at a distance of 1 cm will attract or repel each other with a force of 1 dyne. Thus

$$1 \text{ dyn} = \frac{(1 \text{ esu})^2}{1 \text{ cm}^2}$$

$$\text{or } 1 \text{ esu} = 1 \text{ dyn}^{1/2} \text{ cm} = 1 (\text{g cm s}^{-2})^{1/2} \text{ cm} = 1 (\text{g}^{1/2} \text{ cm}^{3/2} \text{ s}^{-1}) \quad (\text{A1.2})$$

In SI system, the unit of charge is not taken as the fundamental quantity. It is the unit of current that is taken as the fundamental quantity. In this system, a unit of current is the *ampere* which is defined as that current which when flowing through the two infinitely long parallel wires 1 m apart causes an electromagnetic force of  $2 \times 10^{-7}$  N per metre of its length to act on each wire. Since the electrical current is defined as the rate of flow of charge through a conductor, we have

$$I = dQ/dt$$

$$\text{or } dQ = I dt \quad (\text{A1.3})$$

The unit of charge is the *coulomb* (C) which is defined as the amount of charge when 1 ampere of current flows for 1 second. Thus

$$1 \text{ C} = 1 \text{ A} \times 1 \text{ s} \quad (\text{A1.4})$$

### Coulomb's Law

In terms of charges in coulombs, Coulomb's law is written as

$$F = K \frac{Q_1 Q_2}{r^2} \quad (\text{AI.5})$$

where  $K$  is the proportionality constant and is written as

$$K = \frac{1}{4\pi\epsilon} \quad (\text{AI.6})$$

where  $\epsilon$  is the permittivity of the space. For free (empty) space, we write it as  $\epsilon_0$ . The value of the latter as determined from experiment is  $8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$  ( $= 8.854 \times 10^{-12} \text{ C}^2 \text{ kg}^{-1} \text{ m}^{-3} \text{ s}^2$ ).

Consider two 1-C charges separated by 1 m in vacuum. From Eq. (AI.5), we have

$$F = \frac{(1 \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(1 \text{ m})^2} = 8.9876 \times 10^9 \text{ N}$$

Since  $1 \text{ N} = 10^5 \text{ dyn}$ , we have

$$F = 8.9876 \times 10^{14} \text{ dyn}$$

Now substituting the above value of  $F$  and  $r = 100 \text{ cm}$  in Eq. (AI.1) we get

$$8.9876 \times 10^{14} \text{ dyn} = \frac{(1 \text{ C})^2}{(100 \text{ cm})^2}$$

$$\text{or } 1 \text{ C} = 2.9979 \times 10^9 \text{ dyn}^{1/2} \text{ cm} = 2.9979 \times 10^9 \text{ stat C} (= 2.9979 \times 10^9 \text{ esu})$$

We observe that

$$\frac{F_{\text{vacuum}}}{F_{\text{medium}}} = \frac{Q_1 Q_2 / r^2}{Q_1 Q_2 / D r^2} = D$$

$$\frac{F_{\text{vacuum}}}{F_{\text{medium}}} = \frac{Q_1 Q_2 / (4\pi\epsilon_0) r^2}{Q_1 Q_2 / (4\pi\epsilon) r^2} = \frac{\epsilon}{\epsilon_0}$$

Hence, we conclude that

$$D = \frac{\epsilon}{\epsilon_0} = \epsilon_r \quad (\text{AI.7})$$

that is, the dielectric constant is equal to the relative permittivity  $\epsilon_r$ .

Around each charge, an electric field exists because of which another charge placed at a distance experiences a force of attraction or repulsion. The intensity of electric field or the electrical field strength at a point is defined as the force experienced by a unit positive charge at that point. Mathematically, we write

$$E = \frac{F}{Q} \quad (\text{AI.8})$$

The electric field strength of charge  $+Q$  at a distance  $r$  will be given by

$$\frac{F}{Q} = \frac{Q}{Dr^2} \quad (\text{AI.9a})$$

### Relationship between stat Coulomb and Coulomb

$$\text{SI units} \quad E = \frac{Q}{(4\pi\epsilon)r^2} \quad (\text{AI.9b})$$

Since  $F$  is a vector quantity, the electric field  $E$  is also a vector quantity. At a point in space, the electrical field can be represented by an arrow; the length of the arrow is directly proportional to the magnitude of  $E$  and it points towards the charge if  $Q$  is negative and away from it if  $Q$  is positive.

The total electrical field strength all around the charge  $Q$  at a distance  $r$  is given by

$$\left( \begin{array}{l} \text{Electrical field intensity} \\ \text{at a point at a distance} \\ r \text{ from the charge} \end{array} \right) \left( \begin{array}{l} \text{The total area of} \\ \text{cross-section at} \\ \text{the distance } r \end{array} \right) = \frac{4\pi Q}{D} \quad (\text{AI.10a})$$

$$\text{SI units} \quad \left( \frac{Q}{(4\pi\epsilon)r^2} \right) (4\pi r^2) = \frac{Q}{\epsilon} \quad (\text{AI.10b})$$

The dielectric constant  $D$  in CGS-esu units or the relative permittivity (i.e.  $\epsilon/\epsilon_0$ ) in SI units of a substance can be defined in terms of electrical fields as follows.

$$D = \frac{\epsilon}{\epsilon_0} = \frac{\text{Electric field in vacuum}}{\text{Electric field in the given medium}} \quad (\text{AI.11})$$

Instead of describing interactions at a point in terms of the electrical field, it is more convenient to use the electrical potential. The latter is defined as the amount of reversible electrical work done in bringing a unit positive charge from infinity to the point under study. Mathematically, it may be evaluated as follows.

$$V = -w_e = -\int_{\infty}^r F dr$$

$$\text{CGS-esu units} \quad V = -\int_{\infty}^r \frac{Q}{Dr^2} dr = \frac{Q}{Dr} \quad (\text{AI.12a})$$

$$\text{SI units} \quad V = -\int_{\infty}^r \frac{Q}{(4\pi\epsilon)r^2} dr = \frac{Q}{(4\pi\epsilon)r} \quad (\text{AI.12b})$$

The change of potential with distance can be derived by differentiating Eq. (AI.12), such that

$$\text{CGS-esu units} \quad dV = -\frac{Q}{Dr^2} dr = -E dr \quad (\text{AI.13a})$$

$$\text{SI units} \quad dV = -\frac{Q}{(4\pi\epsilon)r^2} dr = -E dr \quad (\text{AI.13b})$$

### Electrical Potential

### Intensity of Electric Field

Equation (A1.13) implies that

$$E = - \frac{dV}{dr}$$

that is, the electrical field intensity is the negative gradient of potential with distance.

### Units of $E$ and $V$

From the expressions

$$E = \frac{F}{Q} \quad (\text{Eq. A1.8})$$

and  $dV = -E dr$

(Eq. A1.4)

we conclude that:

*CGS-esu units*

$E$  has the units of dyn (esu) $^{-1}$

$V$  has the units of (dyn (esu) $^{-1}$ ) (cm) = erg esu $^{-1}$

The unit of electrical potential in CGS-esu system is stat volt (stat V).

Thus 1 stat V = 1 (erg esu $^{-1}$ ) = 1 dyn cm esu $^{-1}$

$$= 1 (\text{g cm s}^{-2}) (\text{cm}) (\text{g}^{1/2} \text{cm}^{3/2} \text{s}^{-1})^{-1}$$

$$= 1 \text{ g}^{1/2} \text{cm}^{1/2} \text{s}^{-1}$$

The following identity for the units of  $E$  may be established.

$$1 \text{ unit of } E \equiv 1 \text{ dyn esu}^{-1} \equiv 1 \text{ erg cm}^{-1} \text{ esu}^{-1} \equiv 1 (\text{stat V}) \text{ cm}^{-1}$$

*SI units*

$E$  has the unit of N C $^{-1}$

$V$  has the unit of (N C $^{-1}$ ) m = J C $^{-1}$

The unit of electrical potential in SI system is volt (V). Thus

$$1 \text{ V} = 1 \text{ J C}^{-1} = 1 (\text{N m}) \text{ C}^{-1} = 1 (\text{kg m s}^{-2}) (\text{m}) (\text{C}^{-1})$$

$$= 1 \text{ kg m}^2 \text{s}^{-2} \text{C}^{-1}$$

The following identity for the unit of  $E$  may be established.

$$1 \text{ unit of } E \equiv 1 \text{ N C}^{-1} \equiv 1 \text{ N (J}^{-1} \text{ V)} \equiv 1 \text{ N (N m)}^{-1} \text{ V} \equiv 1 \text{ V m}^{-1}$$

Since

$$1 \text{ V} = \frac{1 \text{ J}}{1 \text{ C}}$$

$$1 \text{ C} = \frac{1 \text{ J}}{1 \text{ V}}$$

$$\text{we have } 1 \text{ V} = \frac{10^7 \text{ ergs}}{(4.803 \times 10^{-10}) / (1.602 \times 10^{-19}) \text{ esu}}$$

$$\text{or } \frac{1 \text{ erg}}{1 \text{ esu}} = \left( \frac{4.803 \times 10^{-10}}{1.602 \times 10^{-19}} \right) \left( \frac{1}{10^7} \right) (1 \text{ V}) = 300 \text{ V}$$

$$\text{Hence } 1 \text{ stat V} = 300 \text{ V}$$

### Capacitance of the Parallel Plate Capacitor

A capacitor is made up of two parallel metal plates as shown in Fig. A1.1. Let  $d$  be distance between the two plates and let  $A$  be the area of cross-section of each of the two plates. Let a potential difference of  $V$  be generated by connecting the parallel plate capacitor to a battery. Let  $+Q$  and  $-Q$  be the charges generated on the plates.



Fig. A1.1 A capacitor

Thus, charge density on each plate,  $\sigma = \frac{Q}{A}$

The following facts can be derived for the capacitor.

*CGS-esu units*

Electrical field  $E$  generated by the charges in between the plates is

$$E = \frac{4\pi Q}{DA} = \frac{4\pi\sigma}{D} \quad (\text{A1.14a})$$

Potential difference  $V$  between the two plates

$$V = \frac{Q}{Dd} = \left( \frac{Q}{Dd^2} \right) d = E d \quad (\text{A1.15a})$$

Capacitance  $C$  of the capacitor is

$$C = \frac{Q}{V} = \frac{Q}{Ed} = \frac{Q}{(4\pi Q/DA)d} = D \left( \frac{A}{4\pi d} \right) \quad (\text{A1.16a})$$

In vacuum or free space, we will have

$$C_0 = \frac{A}{4\pi d} \quad (\text{A1.17a})$$

*SI units*

$$\text{Electrical field } E = \frac{Q}{\epsilon A} = \frac{\sigma}{\epsilon} \quad (\text{A1.14b})$$

$$\text{Potential difference } V = \frac{Q}{(4\pi\epsilon)d} = \left[ \frac{Q}{(4\pi\epsilon)d^2} \right] d = Ed \quad (\text{A1.15b})$$

$$\text{Capacitance } C = \frac{Q}{Ed} = \frac{Q}{(Q/\epsilon A)d} = \epsilon \left( \frac{A}{d} \right) \quad (\text{A1.16b})$$

$$\text{Capacitance in vacuum, } C_0 = \epsilon_0 \left( \frac{A}{d} \right) \quad (\text{A1.17b})$$

From Eqs (A1.16) and (A1.17), we find that

$$D = \frac{\epsilon}{\epsilon_0} = \frac{C}{C_0} \quad (\text{A1.18})$$

The unit of capacitance is farad.

Since the capacitance is the charge per unit potential, we have

$$1 \text{ F} = \frac{1 \text{ C}}{1 \text{ kg m}^2 \text{s}^{-2} \text{C}^{-1}} = 1 \text{ kg}^{-1} \text{m}^2 \text{s}^2 \text{C}^2$$

### The Magnetic Field

#### A FEW DEFINITIONS REGARDING MAGNETIC FIELD

There exists a magnetic field around a magnet due to which another magnet placed at a distance experiences force of attraction or repulsion. The intensity of magnetic field at a point can be defined by writing an expression for the force between two magnetic poles in a way analogous to the electrical field (Eq. A1.8). However, the 'magnetic pole' is a clumsy and only approximately meaningful concept. Because of this, the magnetic field is defined in terms of its interaction with a moving charge.

The magnetic force on a moving charged particle is known as the *Lorentz force*. If a particle with charge  $Q$  moves with velocity  $v$  through a magnetic field  $B$  acting perpendicular to the direction of velocity, the Lorentz force  $F$  is given by

$$\text{Gaussian system} \quad F = \frac{QvB}{c} \quad (\text{A1.19a})$$

$$\text{SI units} \quad F = QvB \quad (\text{A1.19b})$$

In Gaussian system,  $Q$  is expressed in esu (or stat coulomb),  $v$  and  $c$  (speed of light) in centimetre per second and  $F$  in dynes. The unit of  $B$  in this system is gauss (G). From Eq. (A1.19a), we have

$$1 \text{ G} \equiv 1 \text{ dyn esu}^{-1} \equiv (\text{g cm s}^{-2}) (\text{g}^{1/2} \text{ cm}^{3/2} \text{ s}^{-1})^{-1} \equiv \text{g}^{1/2} \text{ cm}^{-1/2} \text{ s}^{-1} \quad (\text{A1.20})$$

In SI units,  $Q$  is expressed in coulombs,  $v$  in metre per second, and  $F$  in newtons. The unit of  $B$  is tesla (T), also called  $\text{Wb/m}^2$ , where  $\text{Wb}$  stands for weber. From Eq. (A1.19b), we have

$$1 \text{ T} \equiv 1 \text{ N C}^{-1} \text{ m}^{-1} \text{ s} \equiv 1 \text{ kg s}^{-1} \text{ C}^{-1} \quad (\text{A1.21})$$

The magnetic field  $B$  is a vector quantity and is known as magnetic induction or magnetic flux density. The direction of  $B$  can be determined with the help of right-hand rule: If thumb, index finger and middle finger point towards the  $x$ -,  $y$ - and  $z$ -axes in a right-handed coordinate system, then they represent the directions of  $v$  of a positive charge,  $B$  and  $F$ , respectively.

Consider a charge of 1 coulomb flowing perpendicular to a magnetic field of 1 tesla with a velocity of 1 metre per second. The force acting on the charge is

$$F = (1 \text{ C}) (1 \text{ m s}^{-1}) (1 \text{ T})$$

$$\text{Since} \quad 1 \text{ T} = 1 \text{ N C}^{-1} \text{ m}^{-1} \text{ s, we have}$$

$$F = 1 \text{ N} \equiv 10^5 \text{ dyn} \quad (\text{A1.22})$$

In gaussian system, the equivalence of 1 T can be worked out as follows.

$$10^5 \text{ dyn} = \frac{(2.9979 \times 10^9 \text{ esu})(10^2 \text{ cm s}^{-1})(B)}{(2.9979 \times 10^{10} \text{ cm s}^{-1})}$$

$$\text{Thus} \quad B = 10^4 \text{ dyn esu}^{-1} = 10^4 \text{ G} \quad (\text{A1.23})$$

$$\text{Hence} \quad 1 \text{ T} = 10^4 \text{ G} \quad (\text{A1.24})$$

From experiments, we find that the magnetic field at distance  $d$  from a very long straight wire in vacuum carrying a current  $I$  is directly proportional to  $I$  and

inversely proportional to  $d$ , such that

$$B = k \frac{I}{d} \quad (\text{A1.25})$$

where  $k$  is a constant. In the two units mentioned above, the constant  $k$  is described as follows.

$$\text{Gaussian system} \quad k = \frac{2\mu_0}{c} \quad (\text{A1.26a})$$

$$\text{SI units} \quad k = \frac{\mu_0}{2\pi} \quad (\text{A1.26b})$$

where  $\mu_0$  is the permeability of vacuum. The  $\mu_0$  has the following dimensions.

$$\begin{aligned} \text{Gaussian system} \quad 2\mu_0 &= \frac{Bcd}{I} = \frac{Q/l}{I} \\ &= \frac{(\text{g}^{1/2} \text{ cm}^{-1/2} \text{ s}^{-1})(\text{cm s}^{-1})(\text{cm})}{(\text{g}^{1/2} \text{ cm}^{3/2} \text{ s}^{-1})(\text{s}^{-1})} \\ &= \text{Unitless} \end{aligned} \quad (\text{A1.27a})$$

that is,  $\mu_0$  has no units and is assigned a value of 1.

$$\begin{aligned} \text{SI system} \quad \frac{\mu_0}{2\pi} &= \frac{Bd}{I} = \frac{(\text{kg s}^{-1} \text{ C}^{-1})(\text{m})}{\text{C s}^{-1}} \\ &= \text{kg m C}^{-2} = \text{N C}^{-2} \text{ s}^2 \end{aligned} \quad (\text{A1.27b})$$

The unit of  $1 \text{ N C}^{-2} \text{ s}^2$  is also known as *Henry per metre*, and will be equal to  $1 \text{ Wb m}^{-1} \text{ A}^{-1}$ .

Because of the associated magnetic fields, the two electric currents  $I_1$  and  $I_2$  in two parallel rectilinear conductors of length  $l$  separated by a distance  $d$  in vacuum will exert force on each other which is given by the following expression.

$$\begin{aligned} \text{Gaussian system} \quad F &= \left( \frac{Q_2 v}{c} \right) B_1 = \left\{ \frac{Q_2 (l/l)}{c} \right\} B_1 = \left\{ \frac{(Q_2/l)l}{c} \right\} B_1 \quad (\text{Eq. A1.19a}) \\ &= \left( \frac{I_2 l}{c} \right) B_1 \end{aligned}$$

Substituting  $B_1$  from Eq. (A1.25), we get

$$F = \left( \frac{I_2 l}{c} \right) \left( \frac{2 I_1}{c d} \right) = \frac{2 I_1 I_2 l}{c^2 d} \quad (\text{A1.28a})$$

$$\begin{aligned} \text{SI units} \quad F &= (Q_2 v B_1) = Q_2 (l/l) B_1 = (Q_2/l) l B_1 \quad (\text{Eq. A1.19b}) \\ &= I_2 l B_1 \end{aligned}$$

Substituting  $B_1$  from Eq. (A1.25), we get

$$F = (I_2 l) \left( \frac{\mu_0 I_1}{2\pi d} \right) = \left( \frac{\mu_0}{2\pi} \right) \frac{I_1 I_2 l}{d} \quad (\text{A1.28b})$$

### Relationship between Tesla and Gauss Units

### Magnetic Field Produced by an Electric Current

As indicated earlier, Eq. (A1.28b) forms the basis of defining a unit of current (ampere) in SI units. The ampere is defined as that current which when flowing through two long, straight parallel wires exactly one metre apart will exert a force on each other of exactly  $2 \times 10^{-7}$  N per metre of the wire. (One current produces a magnetic field which exerts a force on the moving charges in the other wire). From Eq. (A1.28b), we find that  $\mu_0$  will have the value of

$$\begin{aligned}\mu_0 &= 2\pi (2 \times 10^{-7}) \text{ N A}^{-2} = 4\pi \times 10^{-7} \text{ N C}^{-2} \text{ s}^2 \\ &= 4\pi \times 10^{-7} \text{ T m A}^{-1}\end{aligned}\quad (\text{A1.29})$$

We know that

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$$

$$\mu_0 = 4\pi \times 10^{-7} \text{ N C}^{-2} \text{ s}^2$$

$$\text{Thus } \epsilon_0 \mu_0 = (8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}) (4\pi \times 10^{-7} \text{ N C}^{-2} \text{ s}^2)$$

$$\begin{aligned}&= 1.182 \times 10^{-17} \text{ m}^{-2} \text{ s}^2 \\ &= \frac{1}{(2.9979 \times 10^8 \text{ m s}^{-1})^2} = \frac{1}{c^2}\end{aligned}\quad (\text{A1.30})$$

where  $c$  is the speed of light.

## The Magnetic Field Strength

The vector  $B$  is commonly referred to as the magnetic flux density. Strictly, however, the magnetic field strength  $H$  is a different vector. In vacuum, the two are related to each other as follows.

$$\text{Gaussian system } B = H \quad (\text{A1.31a})$$

The unit of  $H$  is the oersted (Oe), which has the same dimensions as gauss.

$$\text{SI Units } B = \mu_0 H \quad (\text{A1.31b})$$

where  $\mu_0$  is the permeability of the vacuum. The unit of  $H$  may be worked out as follows.

$$\text{Unit of } H = \frac{\text{unit of } B}{\text{unit of } \mu_0} = \frac{\text{N C}^{-1} \text{ m}^{-1} \text{ s}}{\text{N C}^{-2} \text{ s}^2} = \text{C s}^{-1} \text{ m}^{-1} = \text{A m}^{-1}$$

Let a magnetic field strength be 1 oersted. In gaussian units, the magnetic induction will be equal to 1 gauss, i.e.  $10^{-4}$  T. Now with this magnetic induction,  $H$  is SI units will be equal to

$$\begin{aligned}\frac{B}{\mu_0} &= \frac{10^{-4} \text{ T}}{4\pi \times 10^{-7} \text{ T m A}^{-1}} = \frac{1}{4\pi \times 10^{-3}} \text{ A m}^{-1} \\ \text{Thus } 1 \text{ Oersted} &= \frac{1}{4\pi \times 10^{-3}} \text{ A m}^{-1}\end{aligned}\quad (\text{A1.32})$$

## ANNEXURE II Expression of Orientation Polarizability

The potential energy of a molecule having dipole moment  $p$  oriented at an angle  $\theta$  with an electrical field  $E$  is given by

$$V = -pE \cos \theta \quad (\text{AII.1})$$

The number of molecules oriented within the solid angle<sup>†</sup>  $d\omega (= \sin \theta d\theta d\phi)$  as given by Boltzmann distribution is given by

$$dN = Ae^{-V/KT} d\omega = Ae^{pE \cos \theta / KT} \sin \theta d\theta d\phi \quad (\text{AII.2})$$

where  $A$  is a proportionality constant.

The contribution of dipole moment in the direction of the electrical field by the molecules within the solid angle  $d\omega$  is given by

$$\begin{aligned}dp_{\text{contribution}} &= (p \cos \theta) dN \\ &= (p \cos \theta) (Ae^{pE \cos \theta / KT}) \sin \theta d\theta d\phi\end{aligned}\quad (\text{AII.3})$$

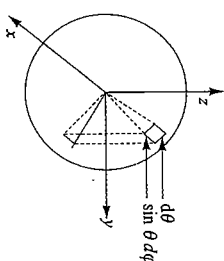
The total contribution in the field direction is

$$\int dp_{\text{contribution}} = Ap \int_0^\pi \int_0^{2\pi} e^{pE \cos \theta / KT} \cos \theta \sin \theta d\theta \int_0^{2\pi} d\phi \quad (\text{AII.4})$$

The average molecular contribution is given by

$$\begin{aligned}P_{\text{av}} &= \frac{\int dp_{\text{contribution}}}{\int dN} \\ &= \frac{Ap \int_0^\pi \cos \theta e^{pE \cos \theta / KT} \sin \theta d\theta \int_0^{2\pi} d\phi}{\int_0^\pi \int_0^{2\pi} e^{pE \cos \theta / KT} \sin \theta d\theta \int_0^{2\pi} d\phi}\end{aligned}\quad (\text{AII.5})$$

<sup>†</sup> By definition, solid angle is equivalent to surface area on a sphere of unit radius. This area is  $(d\theta)(\sin \theta d\phi)$ .



Let  $x = pE/kT$  and  $y = \cos \theta$  such that  $dy = -\sin \theta d\theta$ . With these, Eq. (AII.5) becomes

$$p_{av} = \frac{\int_{-1}^{+1} ye^{-xy} dy}{\int_{-1}^{+1} e^{-xy} dy} \quad (\text{AII.6})$$

Now,

$$\begin{aligned} \int_{-1}^{+1} ye^{-xy} dy &= y \frac{e^{-xy}}{x} \Big|_{-1}^{+1} - \int_{-1}^{+1} \frac{e^{-xy}}{x} dy = y \frac{e^{-xy}}{x} \Big|_{-1}^{+1} - \frac{e^{-xy}}{x^2} \Big|_{-1}^{+1} \\ &= \frac{1}{x} (e^x + e^{-x}) - \frac{1}{x^2} (e^x - e^{-x}) \end{aligned}$$

$$\int_{-1}^{+1} e^{-xy} dy = \frac{e^{-xy}}{x} \Big|_{-1}^{+1} = \frac{1}{x} (e^x - e^{-x})$$

$$\text{Hence, } p_{av} = p \left( \frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} \right) = p \left( \coth x - \frac{1}{x} \right) \quad (\text{AII.7})$$

The function

$$\mathcal{L}(x) = \coth x - \frac{1}{x}$$

is known as the Langevin function. The quantity  $x (= pE/kT)$  has a small value. For this, we can write

$$\coth x = \frac{1}{\tanh x} = \frac{1}{x - x^3/3} = \frac{1}{x} (1 - x^2/3)^{-1} = \frac{1}{x} (1 + x^2/3)$$

With this, Eq. (AII.8) becomes

$$p_{av} = p \left[ \frac{1}{x} \left( 1 + \frac{x^2}{3} \right) - \frac{1}{x} \right] = p \left( \frac{x}{3} \right) = \frac{p^2}{3kT} E \quad (\text{AII.9})$$

Thus, the term  $p^2/3kT$  plays the proportionality factor between  $p_{av}$  and  $E$ . This may be identified with the orientation polarizability.

# 4 Molecular Spectroscopy

## 4.1 INTRODUCTION

### Absorption and Emission Spectra

The subject of molecular spectroscopy deals with the interaction of electromagnetic radiations with the matter. The absorption (or emission) of electromagnetic radiations by a molecule is highly selective and follows the relation

$$\Delta E = h\nu = E_2 - E_1 \quad (4.1.1)$$

where  $\nu$  is the frequency of radiation absorbed, and  $E_1$  and  $E_2$  are the lower and higher energies of molecular levels, respectively. Thus, the molecule is excited from a lower molecular energy level to the higher one when it absorbs radiation. In emission of radiation, the reverse of the above is observed.

It is possible to correlate the experimentally observed data on absorption or emission with the nature of molecular changes which are responsible for the absorption or emission. With the help of these correlations, much useful information regarding the size, shape, flexibility of the bond and electronic arrangements of a molecule can be deduced. Before considering such correlations, a brief discussion on different types of molecular energies is in order.

A molecule possesses many forms of energies. These are:

- Translational energy ; by virtue of its translatory motion.
- Rotational energy ; by virtue of bodily rotation of a molecule about its centre of gravity.
- Vibrational energy ; by virtue of the periodic displacement of its atoms from their equilibrium positions.
- Electronic energy ; by virtue of different electronic arrangements in the molecule.

It was seen in Chapters 1 and 2 that the energies listed above are all quantized, i.e. a molecule cannot have any arbitrary energies of rotation, vibration or electronic, but can exist only in the allowed energy levels. According to the Born-Oppenheimer approximation, the energies listed above can be treated separately and we can write the total energy of the molecule as

$$E_{\text{total}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}}$$

where  $E_{\text{trans}}$ ,  $E_{\text{rot}}$ ,  $E_{\text{vib}}$  and  $E_{\text{el}}$  represent translational, rotational, vibrational and electronic energies, respectively. In general

$$E_{\text{el}} \gg E_{\text{vib}} \gg E_{\text{rot}} \gg E_{\text{trans}}$$

The approximate difference between the two levels of any one of these energies may be worked out from the following expressions.

$$E_{\text{trans}} = n^2 \left( \frac{h^2}{8ml^2} \right)$$

where  $n$  is the translational quantum number and has integral values 1, 2, 3, 4, ...

$$E_{\text{rot}} = J(J+1) \frac{h^2}{8\pi^2 I}$$

where  $J$  is the rotational quantum number. The permitted values of  $J$  are 0, 1, 2, 3, ...

$$E_{\text{vib}} = \left( v + \frac{1}{2} \right) \frac{h}{2\pi} \sqrt{\frac{k_s}{\mu}}$$

where  $v$  is the vibrational quantum number and possesses values of 0, 1, 2, 3, ...

$$E_{\text{el}} = - \frac{2\pi^2 e^4 Z^2}{(4\pi\epsilon_0)^2 n^2 h^2}$$

where  $n$  is the electronic quantum number and has values 1, 2, 3, 4, ...

### Exclusion of Translational Spectroscopy

At the very outset, an important conclusion regarding the energy difference between the two translational levels may be stated. The energy difference between the two successive translational levels is of the order of  $10^{-60}$  J mol<sup>-1</sup> for a normal molecule moving in a container of ordinary size. This separation is too small to be determined experimentally. It is for this reason that the translational energy is considered to vary continuously and thus the corresponding translational spectroscopy to be observed is completely excluded.

### Order of Energy Difference

The order of energy difference between the two successive energy levels for other motions along with the approximate wavelengths of radiation to be employed for the required transitions are shown in Table 4.1.1.

**Table 4.1.1** Energy Difference between the Two Successive Energy Levels

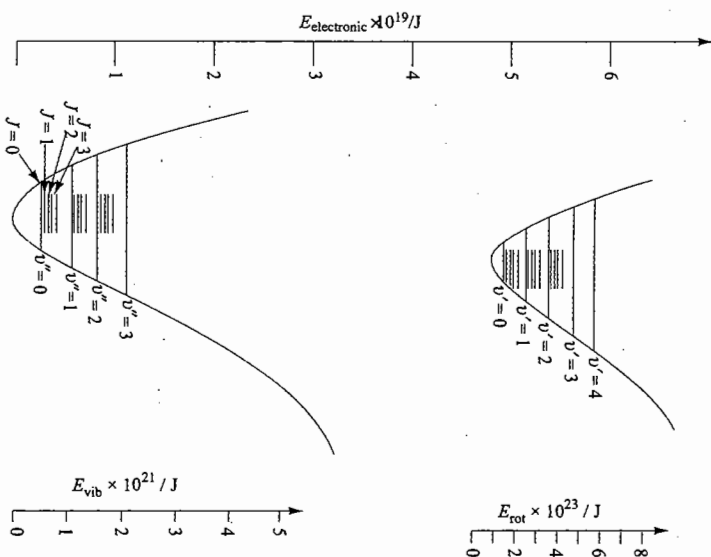
Motion	$\approx \Delta E/J$ molecule <sup>-1</sup>	$\approx \lambda/m$
Rotation	$10^{-23}$	$10^{-2}$
Vibration	$10^{-21}$	$10^{-4}$
Electronic	$10^{-19}$	$10^{-6}$

From Table 4.1.1, it follows that the separation between the two electronic energy levels is larger than that between the two vibrational energy levels, which in turn, is larger than that between the two rotational levels.

### Diagrammatic Representation of Energy Levels

It is customary to show the different energy separations in a diatomic molecule by a diagram shown in Fig. 4.1.1. Each stable electronic level exhibits a minimum in the potential energy diagram. The upper level relative to the ground level has a smaller depth which lies at a larger internuclear distance. In the minimum valley, the different vibrational and rotational levels are shown by straight lines. The vibrational energy levels are almost equidistant (strictly true only for a harmonic

**Fig. 4.1.1 A**  
Schematic representation of various energy levels



In Fig. 4.1.1 only a few energy levels have been shown. In fact, a very large number of vibrational levels going up to the dissociation limit exist for each electronic level. Similarly, a series of rotational levels exist with each of the vibrational level.

Transitions between rotational levels belonging to a particular vibration level are observed in the microwave region of the electromagnetic spectrum ( $\lambda \approx 10^{-2}$  to  $10^{-4}$  m); these are called *pure rotational spectra*. Transitions between vibrational levels within the same electronic state lie in the infrared region ( $\lambda \approx 10^{-4}$  to  $10^{-6}$  m) and are responsible to exhibit *pure vibrational and vibrational-rotational spectra*. Finally, transitions between electronic levels give rise to the spectra in the visible or ultraviolet region ( $\lambda \approx 10^{-6}$  to  $10^{-9}$  m) and are called *electronic spectra*.

In addition to the various spectra listed above, there exist two other important spectra which lie in the radiofrequency region of the spectrum (10 m to 1 cm wavelength). These are connected with the reversal of spin of a nucleus and an electron, and are known as *nuclear magnetic resonance spectrum* and *electron-spin resonance spectrum*, respectively.



Lastly, we may mention another type of spectroscopy which is known as *Raman spectroscopy*. This yields information similar to that obtained in microwave and infrared regions. The incident light used in this spectroscopy lies in the visible region. Figure 4.1.2 depicts a schematic diagram of the various electromagnetic spectra listed.

In the following sections, we describe the different types of spectroscopy in the increasing magnitude of energy of absorbed or emitted electromagnetic radiations.

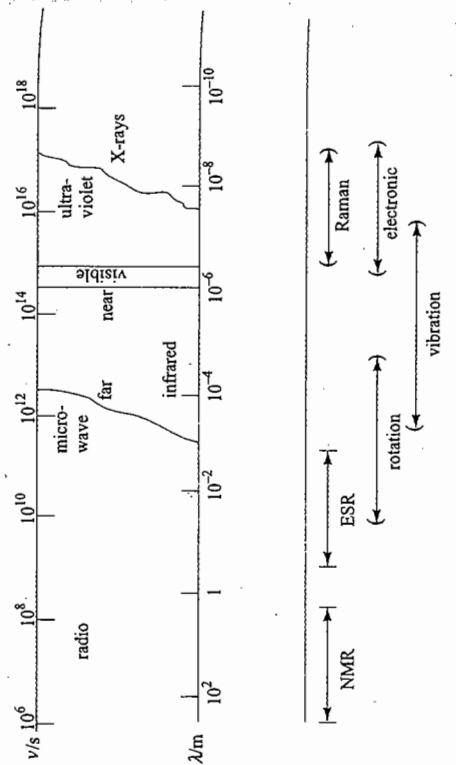


Fig. 4.1.2 Schematic diagram of electromagnetic spectra

The absorption of microwave, infrared, visible, and ultra-violet radiations by a gaseous or liquid sample is often expressed by the Beer-Lambert law:

$$\log \frac{I}{I_0} = -\epsilon lc \quad (4.1.2)$$

where  $c$  and  $l$  are the concentration and path length of the sample,  $I_0$  and  $I$  are the intensities of incident and transmitted light, and  $\epsilon$  is the molar absorption coefficient which has a characteristic value for a particular absorption of a molecule.

The absorption of a photon of frequency  $\nu$  by a molecule causes a transition from the lower energy state  $m$  to the higher energy state  $n$  provided the following expression is satisfied:

$$E_n - E_m = h\nu$$

The above transition is caused by the interaction of the oscillating electric field of the radiation with the electrical charges of the molecule. The quantum-mechanical treatment shows that the probability of absorption or emission between the two stationary states  $m$  and  $n$  is proportional to the square of *transition moment integral* defined as

$$P_{mn} = \int \psi_m^* P_{op} \psi_n d\tau \quad (4.1.3)$$

where  $P_{op}$  is the electric dipole-moment operator and is given by

$$P_{op} = \sum_i Q_i r_i \quad (4.1.4)$$

The integration in Eq. (4.1.3) is carried over the full range of electronic and nuclear coordinates. Of many possible transitions, only those transitions are allowed for which  $P_{mn}$  is nonzero. The transitions having  $P_{mn} = 0$  are forbidden. The condition(s) stating the difference of quantum numbers of involved stationary states in a transition is (are) known as *selection rule(s)*.

The actual expression of the probability of absorption of radiation is known as *Einstein absorption coefficient* and is given by

$$B_{mn} = \frac{8\pi^2}{h^2} P_{mn} \quad (4.1.5)$$

The coefficient  $B_{mn}$  is related to the molar absorption coefficient  $\epsilon$ . Since an actual absorption is spread over a region of wavelength, the  $B_{mn}$  is related to the integral intensity  $\int \epsilon d\nu$  through the expression

$$\int \epsilon d\nu = \frac{hN_A \tilde{\nu}_0}{(2.303)(10^3)^2 c^2} B_{mn} \quad (4.1.6)$$

where  $c$  is the speed of radiation and  $\tilde{\nu}_0$  is the wavenumber of a band maximum.

It is conventional to take as the ideal case of the transition of electronic mass between  $\nu = 0$  to  $\nu = 1$  states of a harmonic oscillator. For this,  $B_{mn}$  is given by

$$B_{mn} = \frac{\pi e^2}{(hm \tilde{\nu}_0)} \quad (4.1.7)$$

and the transition probability is given by

$$(\int \epsilon d\nu)_{\text{ideal}} = \frac{\pi(e^2/4\pi\epsilon_0)N_A}{(2.303)(10^3)^2 mc^2} = 2.31 \times 10^6 \text{ m mol}^{-1} \quad (4.1.8)$$

The oscillator strength  $f$  of a given transition is defined as the ratio of actual and ideal transition probabilities, such that

$$f = \frac{(\int \epsilon d\nu)_{\text{actual}}}{(\int \epsilon d\nu)_{\text{ideal}}} = (4.33 \times 10^{-7} \text{ mol m}^{-1}) (\int \epsilon d\nu)_{\text{actual}} \quad (4.1.9)$$

The area under an absorption band gives either  $B_{mn}$  through Eq. (4.1.6) or  $f$  through Eq. (4.1.9).

From the expression of transition moment (Eq. 4.1.3) often some very important statements can be deduced qualitatively regarding the possibility of an induced transition by the radiation. For an illustration, the system of particle in a box is considered here. Let the particle be an electron and let the balancing positive charge

### Qualitative Derivation of Selection Rule for Particle in a Box

be located at the mid-point of the box. A few wave functions of the present system are shown in Fig. 4.1.3. The symmetry of the wave functions with respect to the centre of the box are also depicted in Fig. 4.1.3. These wave functions may be classified into the following two categories.

*Symmetric (or even) functions* where  $\psi(y) = \psi(-y)$

*Antisymmetric (or odd) functions* where  $\psi(y) = -\psi(-y)$

From Fig. 4.1.3, it may be concluded that the functions  $\psi_1, \psi_3, \psi_5, \dots$ , etc., are symmetric functions whereas the functions  $\psi_2, \psi_4, \psi_6, \dots$ , etc., are antisymmetric functions.

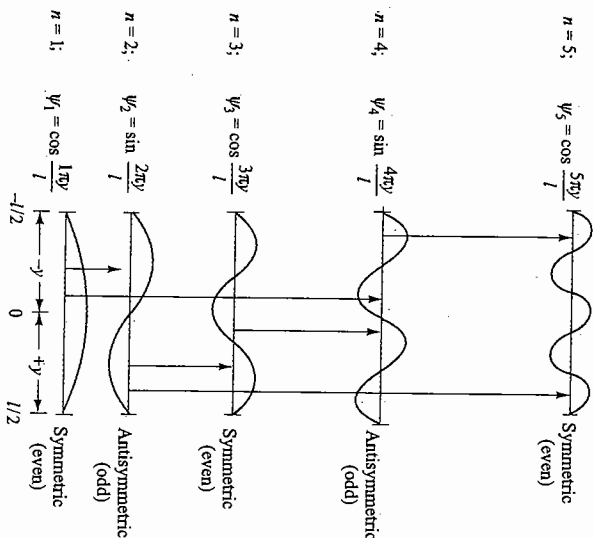


Fig. 4.1.3 Symmetric and antisymmetric wave functions of particle in a box and some of the allowed transitions

The dipole moment of the system is given by

$$p = ey$$

where  $y$  is the distance of the electron from the centre of the box. For an observable transition from a state  $n$  to a state  $m$ , we must have

$$P_{nm} = \int_{-l/2}^{+l/2} \psi_n(ey) \psi_m dy \neq 0 \quad (4.1.10)$$

Without actually carrying out the above integration, we can derive the selection rules by studying the symmetry of the three functions  $\psi_n, \psi_m$  and  $(ey)$ . If the product of these three functions is an odd function, the result of the integral from  $-l/2$  to  $0$  will exactly cancel the contribution from  $0$  to  $l/2$ , and thus  $P_{nm}$  will be equal to zero. The dipole moment operator is an odd function and thus a transition from an odd function to an odd function or from an even function to an even function will lead to  $P_{nm}$  equal to zero and hence such transitions will not be

### Quantitative Derivation of Selection Rule for Particle in a Box

permissible. However, for a transition from an even function to an odd function or vice versa, the expression  $\psi_n(ey)\psi_m$  will be even and thus  $P_{nm}$  will be nonzero. Consequently, such a transition will be allowed. The above guidelines may be summarized as follows.

$$\left. \begin{array}{l} \psi_{\text{even}} \rightarrow \psi_{\text{odd}} \\ \psi_{\text{odd}} \rightarrow \psi_{\text{even}} \end{array} \right\} \text{allowed}$$

$$\left. \begin{array}{l} \psi_{\text{even}} \rightarrow \psi_{\text{even}} \\ \psi_{\text{odd}} \rightarrow \psi_{\text{odd}} \end{array} \right\} \text{forbidden}$$

Hence, the selection rule for a particle in a box is  $\Delta n = \pm 1, \pm 3, \pm 5, \dots$ . Some of the allowed transitions are shown in Fig. 4.1.3.

The coordinate system of particle in a box discussed in Section 1.4 is related to that shown in Fig. 4.1.3 by the relation

$$y = x - \frac{l}{2}$$

Hence, the dipole moment operator is

$$p = ey = e \left( x - \frac{l}{2} \right)$$

The wave functions are given by the expression

$$\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$$

The expression of transition moment is

$$P_{nm} = \frac{2e}{l} \int_0^l \left( \sin \frac{n\pi x}{l} \right) \left( \sin \frac{m\pi x}{l} \right) \left( x - \frac{l}{2} \right) dx$$

Since the functions are orthogonal, the integral arising from the  $l/2$  term will be zero and thus we may write  $P_{nm}$  as

$$P_{nm} = \frac{2e}{l} \int_0^l \left( \sin \frac{n\pi x}{l} \right) \left( \sin \frac{m\pi x}{l} \right) (x) dx$$

Making use of relations

$$\sin \theta \sin \phi = \frac{1}{2} [\cos(\theta - \phi) - \cos(\theta + \phi)]$$

$$\text{and } \int x \cos ax \, dx = \frac{1}{a^2} \cos ax + \frac{x}{a} \sin ax$$

$$\text{we get } P_{nm} = \frac{el}{\pi^2} \left[ \frac{\cos[(n-m)\pi] - 1}{(n-m)^2} - \frac{\cos[(n+m)\pi] - 1}{(n+m)^2} \right]$$

where the sine terms have been ignored since  $n-m$  and  $n+m$  are integers. If  $n$  and  $m$  are both even numbers or both odd numbers, then  $n-m$  and  $n+m$  are

even numbers and hence these will lead to  $p_{nm} = 0$ ; consequently, such transitions will be forbidden. If  $n$  is even and  $m$  is odd or vice versa, then  $n - m$  and  $n + m$  are odd and thus  $p_{nm}$  is nonzero; consequently, such transitions are allowed. Thus, the selection rule in the present case is that  $n - m$  should be an odd number, i.e.  $\Delta n = \pm 1, \pm 3, \pm 5, \dots$

### Selection Rule for a Harmonic Oscillator

The harmonic-oscillator wave functions are given by

$$\psi_n = \left( \frac{\sqrt{\alpha}}{2^n n! \sqrt{\pi}} \right)^{1/2} \exp(-y^2/2) H_n; \quad \text{where } y = \sqrt{\alpha} x \quad (\text{Eq. 1.5.11})$$

From this, we can write

$$y\psi_n = \left( \frac{\sqrt{\alpha}}{2^n n! \sqrt{\pi}} \right)^{1/2} \exp(-y^2/2) (yH_n)$$

Since  $yH_n = nH_{n-1} + (1/2)H_{n+1}$ , we get

$$y\psi_n = \left( \frac{\sqrt{\alpha}}{2^n n! \sqrt{\pi}} \right)^{1/2} \exp(-y^2/2) \left[ nH_{n-1} + \frac{1}{2}H_{n+1} \right]$$

Since  $y = \sqrt{\alpha}x$ , we can write the above expression as

$$\begin{aligned} x\psi_n &= \left( \frac{n}{2\alpha} \right)^{1/2} \left( \frac{\sqrt{\alpha}}{2^{n-1}(n-1)! \sqrt{\pi}} \right)^{1/2} \exp(-y^2/2) H_{n-1} \\ &\quad + \left( \frac{n+1}{2\alpha} \right)^{1/2} \left( \frac{\sqrt{\alpha}}{2^{n+1}(n+1)! \sqrt{\pi}} \right)^{1/2} \exp(-y^2/2) H_{n+1} \\ &= \left( \frac{n}{2\alpha} \right)^{1/2} \psi_{n-1} + \left( \frac{n+1}{2\alpha} \right)^{1/2} \psi_{n+1} \end{aligned}$$

With this, the expression of transition moment integral  $\langle \psi_m | qx | \psi_n \rangle$  becomes

$$\begin{aligned} q \langle \psi_m | x | \psi_n \rangle &= q \langle \psi_m | \left[ \left( \frac{n}{2\alpha} \right)^{1/2} \psi_{n-1} + \left( \frac{n+1}{2\alpha} \right)^{1/2} \psi_{n+1} \right] \rangle \\ &= q \left[ \left( \frac{n}{2\alpha} \right)^{1/2} \langle \psi_m | \psi_{n-1} \rangle + \left( \frac{n+1}{2\alpha} \right)^{1/2} \langle \psi_m | \psi_{n+1} \rangle \right] \end{aligned}$$

Using the orthonormality of Hermite polynomials, we can write

$$\langle \psi_m | x | \psi_n \rangle = \left( \frac{n}{2\alpha} \right)^{1/2} \delta_{m,n-1} + \left( \frac{n+1}{2\alpha} \right)^{1/2} \delta_{m,n+1}$$

where  $\delta$  stands for Kronecker delta ( $\delta_{mn} = 1$  if  $m = n$  otherwise zero).

Thus, the allowed electric-dipole transitions for the harmonic oscillator involve a change of  $\pm 1$  in the quantum number.

The selection rule for a rigid rotator can be derived similarly and are found to be  $\Delta J = \pm 1$ , respectively, (see page 450).

## 4.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The nuclear magnetic resonance spectroscopy (NMR) which lies in the radiofrequency region of electromagnetic radiation is found to be very useful for the structural elucidation of molecules, especially in the domain of organic molecules. We now discuss the various aspects of NMR spectroscopy.

The nuclear magnetic resonance spectroscopy basically deals with the interaction of nuclei with the external magnetic field. The main constituents of a nucleus are protons and neutrons. A proton carries a unit positive charge whereas the neutron is an uncharged entity. Both these particles spin around their own axis with the same spin quantum number  $1/2$ .

The value of angular momentum associated with each of these spins is

$$\sqrt{\frac{1}{2} \left( \frac{1}{2} + 1 \right)} \left( \frac{h}{2\pi} \right) = \frac{\sqrt{3}}{2} \left( \frac{h}{2\pi} \right)$$

Each nucleus possesses a total spin quantum number which results simply from the vector addition of the spins of its protons and neutrons. Some empirical rules based on experimental facts regarding the total spin quantum number are available. These are:

- Nuclei having both charge number and mass number even (i.e. having both protons and neutrons even in number) have zero spin quantum number. Examples include  $^4_2\text{He}$ ,  $^{12}_6\text{C}$  and  $^{16}_8\text{O}$ .
- Nuclei having odd charge number and even mass number (i.e. both protons and neutrons are odd in nature) have integral spin quantum number. Examples include  $^2_1\text{H}$ ,  $^{14}_7\text{N}$  (spin = 1) and  $^{10}_5\text{B}$  (spin = 3).
- Nuclei with odd mass number have half-integral spin. Examples include  $^1_1\text{H}$ ,  $^{15}_7\text{N}$  (spin =  $1/2$ ),  $^{17}_8\text{O}$  (spin =  $5/2$ ),  $^{19}_9\text{F}$  (spin =  $1/2$ ) and  $^{35}_{17}\text{Cl}$  (spin =  $3/2$ ).

The magnitude of angular momentum vector  $L$  associated with the spinning of a nucleus having total spin quantum number  $I$  is given by

$$L = \sqrt{I(I+1)} \frac{h}{2\pi} \quad (4.2.1)$$

According to quantum mechanics, the angular momentum vector cannot have any arbitrary direction but can point only along certain directions (space quantization of the angular momentum vector). These directions are such that the component of angular momentum vector along a certain reference axis, known as the  $z$ -axis, has only quantized values. This reference axis is usually taken to be the direction of an external magnetic field. The permitted values of components of angular momentum along the  $z$ -axis are given by the expression  $m_I(h/2\pi)$ , where  $m_I$  can take the following values:

$$m_I = I, (I-1), \dots, -(I-1), -I \quad (4.2.2)$$

There are a total of  $(2I+1)$  components in each case. These components are normally degenerate (i.e. all of them have same energy). This degeneracy is lifted up in the presence of a magnetic field and we will see shortly that the NMR is basically due to the lifting up of degeneracy of these energy levels.

### Magnetic Moment of the Nucleus

The spinning of a nucleus is equivalent to the circulation of a positive charge around the axis of spinning. This, in turn, produces a tiny magnet placed along the spin axis. The magnetic moment of the generated magnet can be calculated with the help of Ampere's law:

$$\mu_m = iA \quad (4.2.3)$$

where  $i$  is the current circulating in the coil per unit time,  $A$  is the area of cross-section of the coil.

If  $r$  is the radius of the coil and  $v$  is the velocity with which charge is spinning, then

$$i = (\text{Number of revolutions per unit time}) \times (\text{Positive charge on the nucleus})$$

$$= \frac{v}{2\pi r} (e)$$

$$\text{and } A = \pi r^2$$

Substituting these expressions in Eq. (4.2.3), we get

$$\mu_m = iA = \left( \frac{ve}{2\pi r} \right) (\pi r^2)$$

$$\cong (vr) \frac{e}{2} = (m_p vr) \left( \frac{e}{2m_p} \right) = L \left( \frac{e}{2m_p} \right) \quad (4.2.4)$$

Thus, the value of the magnetic momentum vector is  $(e/2m_p)$  times the value of the angular momentum vector. Since the charge on the nucleus is positive, it follows from Eq. (4.2.4) that both angular and magnetic momentum vectors point towards the same direction.

Experimentally, it is found that Eq. (4.2.4) is not applicable as such but requires the addition of one more factor,  $g$ . This factor is known as the *nuclear splitting factor* or simply the *nuclear  $g$  value*. The numerical value of  $g$  cannot be calculated theoretically and thus is determined from the experimental data. With this, Eq. (4.2.4) becomes

$$\mu_m = g \left( \frac{e}{2m_p} \right) L \quad (4.2.5)$$

Substituting the expression of  $L$  from Eq. (4.2.1) in Eq. (4.2.5), we get

$$\mu_m = g \left( \frac{eh}{4\pi m_p} \right) \sqrt{I(I+1)} \quad (4.2.6)$$

The basic unit of magnetic moment is defined as

$$\mu_N = \left( \frac{eh}{4\pi m_p} \right) \quad (4.2.7)$$

The basic unit  $\mu_N$  is called the *nuclear magneton*. Its value for the hydrogen nucleus is

$$\mu_N = \frac{eh}{4\pi m_p} = \frac{(1.602 \times 10^{-19} \text{ C})(6.626 \times 10^{-34} \text{ J s})}{4(22/7)(1.673 \times 10^{-27} \text{ kg})}$$

$$= 5.047 \times 10^{-27} \text{ J T}^{-1} \quad (4.2.8)$$

### Potential Energy of a Nucleus in a Magnetic Field

$$V = -B\mu_z$$

Potential energy  $V$  of a nucleus placed in a magnetic field  $B$  is given by the relation

$$V = -B\mu_z \quad (4.2.9)$$

where  $\mu_z$  is the  $z$ -component of the magnetic momentum vector. Let  $\theta$  be the angle between the magnetic momentum vector and the  $z$ -axis, then

$$\mu_z = \mu_m \cos \theta \quad (4.2.10)$$

Substituting Eq. (4.2.6) in Eq. (4.2.10), we get

$$\mu_z = \left( g \mu_N \sqrt{I(I+1)} \right) \cos \theta \quad (4.2.11)$$

The angle  $\theta$  cannot have any arbitrary value, but only a few allowed discrete values which satisfy the condition of quantization of the component of angular momentum vector along the axis of magnetic field, i.e.

$$\left( \sqrt{I(I+1)} \frac{h}{2\pi} \right) \cos \theta = m_l \frac{h}{2\pi}$$

$$\text{or } \sqrt{I(I+1)} \cos \theta = m_l \quad (4.2.12)$$

Substituting Eq. (4.2.12) in Eq. (4.2.11), we get

$$\mu_z = g \mu_N m_l$$

Substituting the above relation in Eq. (4.2.9), we have

$$V = -B(g \mu_N m_l) \quad (4.2.13a)$$

that is, the potential energy of interaction of a nucleus with external magnetic field depends on the value of  $m_l$ . Equation (4.2.13a) is usually written as

$$V = -\gamma \frac{h}{2\pi} B m_l \quad (4.2.13b)$$

where  $\gamma = 2\pi g \mu_N / h$  and is known as *gyromagnetic ratio* (see Eq. 4.2.18).

Three cases may be distinguished.

1. The potential energy increases with increase in magnetic field for negative value of  $m_l$ . This is due to the fact that the orientation of the poles of tiny magnet generated due to the spinning of the nucleus is in the unfavourable position, i.e. the north pole of the tiny magnet is near to the north pole of external magnet and the south pole is near to the south pole. This arrangement leads to more and more repulsion (or destabilization) as the external magnetic field is increased.

2. The potential energy decreases with increase in magnetic field for positive value of  $m_l$ . Here the orientation of tiny magnet is in the favourable direction, i.e. the north pole of the tiny magnet is near to the south pole of the external magnetic field and vice versa. This leads to more and more attraction (or stabilization) as the external magnetic field is increased.

3. The potential energy remains unchanged for a zero value of  $m_l$ . Here the orientation of tiny magnet is in the perpendicular direction of the external magnetic field.

### Potential Energy of a Proton in a Magnetic Field

The value of spin quantum number for protons is  $+1/2$ . Thus,  $m_l$  can have two values of  $+1/2$  and  $-1/2$ . The schematic variations of potential energies of  $\alpha$  and  $\beta$  protons are shown in Fig. 4.2.1.

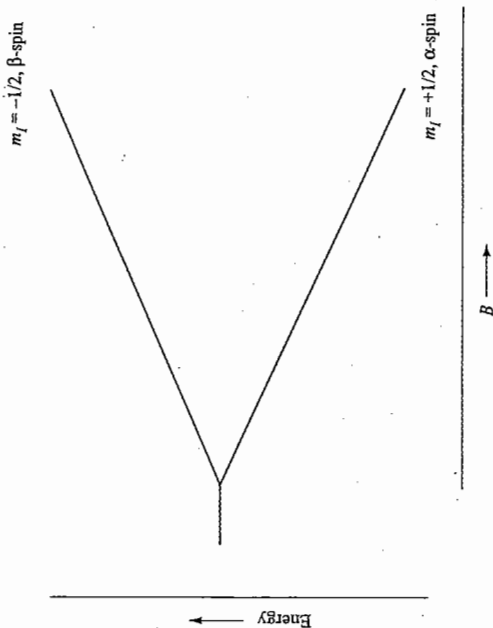


Fig. 4.2.1 Variations of potential energies of  $\alpha$  and  $\beta$  protons in the presence of increasing magnetic field

The value of  $g$  for protons is found to be 5.585 4. Substituting the values of  $m_l$  and  $g$  along with  $\mu_N$  from Eq. (4.2.8), we get

$$V_{+1/2} = -(5.047 \times 10^{-27} \text{ J T}^{-1}) (5.585 \text{ 4}) (1/2) B$$

$$= -(1.410 \times 10^{-26} \text{ J T}^{-1}) B$$

$$V_{-1/2} = -(5.047 \times 10^{-27} \text{ J T}^{-1}) (5.585 \text{ 4}) (-1/2) B$$

$$= + (1.410 \times 10^{-26} \text{ J T}^{-1}) B$$

The energy difference between the two levels as given by Eq. (4.2.13a) is

$$\Delta V = \mu_N g B \quad (4.2.14)$$

$$= (2.820 \times 10^{-26} \text{ J T}^{-1}) B \quad (4.2.15)$$

In terms of frequency unit, we have

$$\nu = \frac{(2.820 \times 10^{-26} \text{ J T}^{-1}) B}{6.626 \times 10^{-34} \text{ J s}} = (4.26 \times 10^7 \text{ T}^{-1} \text{ s}^{-1}) B \quad (4.2.16)$$

Thus, a proton in the lower energy level ( $m_l = 1/2$ ) can be promoted to the higher energy level ( $m_l = -1/2$ ) in the presence of a magnetic field by supplying the necessary energy in the form of electromagnetic radiation of frequency equal to  $\{4.26 \times 10^7 \text{ Hz (B/T)}\}$ . Such type of transitions is the subject of NMR spectroscopy and if protons are involved, it may be called *proton magnetic resonance (PMR)* spectroscopy. The frequency associated with such a transition depends on the strength of the magnetic field experienced by the nucleus undergoing the transition.

### Magnetic Active and Inactive Nuclei

### Intensity of NMR Signals

The magnitude of the magnetic field normally used is 1 tesla. For this field strength, the frequency of radiation required for the reversal of the spin of proton is

$$\nu = (4.26 \times 10^7 \text{ T}^{-1} \text{ s}^{-1}) (1 \text{ T}) = 42.6 \times 10^6 \text{ Hz} = 42.6 \text{ MHz} \quad (4.2.17)$$

The above frequency lies in the radiofrequency region of the electromagnetic spectrum ( $3 \times 10^6 - 3 \times 10^{10} \text{ Hz}$ ).

The energy difference between the two nuclear levels can also be expressed in the unit of angular frequency  $\omega$  (expressed as radians/second). Since  $\omega = 2\pi\nu$ , we have

$$\omega = 2\pi\nu = 2\pi \left( \frac{\mu_N g}{h} B \right) = \left( \frac{2\pi \mu_N g}{h} \right) B = \gamma B \quad (4.2.18)$$

where  $\gamma$  is the nuclear constant and is known as the *gyromagnetic ratio* or the *magnetogyric ratio*.

It may be mentioned here that the absorption of radiation of a suitable wavelength when a nucleus is placed in a magnetic field occurs only for those nuclei which have nonzero spin angular momentum. Such types of nuclei are known as *magnetic active nuclei*. Magnetic inactive nuclei have zero spin quantum number, *vis-à-vis*, zero magnetic moment. Such type of nuclei cannot interact with the external magnetic field and thus do not show any absorption of radiation. Examples include  $^{12}\text{C}$  and  $^{16}\text{O}$ .

The excitation of a nucleus from the lower energy level to the higher one can occur only if the lower level is more populated than the higher one. The relative populations of nuclei over the available energy levels can be calculated from the Boltzmann equation

$$\frac{n_2}{n_1} = \exp(-\Delta V/kT) \quad (4.2.19)$$

when  $n_1$  and  $n_2$  are the number of nuclei in the lower and higher energy levels, respectively,  $\Delta V$  is the energy difference between these two levels and  $k$  is the Boltzmann constant ( $k = R/N_A$ ).

A given system with the minimum potential energy is the most stable one. Thus, it may be expected that the most stable arrangement of nuclei in the magnetic field would be one in which all nuclei occupy the lowest energy level. Take, for example, the system consisting of protons only. Energetically, the system would have been most stable where all the protons occupy the lowest energy level (i.e. all protons have  $\alpha$ -spins). The only factor which opposes this arrangement is the value of thermal energy relative to that of energy difference between the two levels. If  $\Delta V$  is much larger than  $kT$ , then the lowest energy level is densely populated. The upper levels do contain some nuclei though their actual number is insignificant. This number decreases rapidly as  $\Delta V$  becomes larger and larger. On the other hand, if  $\Delta V$  is much smaller than  $kT$ , the upper levels are also equally populated; nevertheless, the population in the lowest level is still larger than those in the upper levels. The two levels will have the same population only when the term  $\Delta V/kT$  in Eq. (4.2.19) has a zero value. This is possible only when the temperature

of the system is infinite—an impossible proposition. Thus, it may be concluded that the lowest level is always more populated than the upper level.

Let us calculate the relative population of protons in the two available energy levels at room temperature (300 K) under the influence of 10 000 gauss (i.e. 1 tesla)

$$\Delta V = (2.820 \times 10^{-26} \text{ J T}^{-1}) (1 \text{ T}) = 2.820 \times 10^{-26} \text{ J} \quad (\text{Eq. 4.2.15})$$

$$kT = (1.38 \times 10^{-23} \text{ J K}^{-1}) (300 \text{ K}) = 4.14 \times 10^{-21} \text{ J}$$

$$\frac{n_2}{n_1} = \exp(-\Delta V/kT) = \exp\{(-2.820 \times 10^{-26} \text{ J})/(4.14 \times 10^{-21} \text{ J})\}$$

$$= \exp(-6.81 \times 10^{-6}) \approx 0.999\,993$$

Thus if ground level, for example, contains  $10^6$  molecules, then the upper level will contain  $0.999\,993 \times 10^6$  molecules. Hence, there exists a population difference of about 7 molecules out of a total of  $10^6 + 0.999\,993 \times 10^6$  molecules (i.e. 2 million molecules).

Transition from one level to another can take place in either directions, i.e. the nucleus can be promoted from the lower energy level to the upper one (upward transition) with the absorption of radiation and also it can come back from the upper level to the lower level (downward transition) with the emission of radiation. Statistically, it may be expected that the rate at which transitions from a level takes place depends on the population of the level. Thus, it may be concluded that the upper transitions are more than the downward transitions and hence there occurs a net absorption.

The intensity of net absorption depends on the difference between the populations of particles in the two involved levels. In the case of NMR, this difference is small and thus the intensity of absorption is also small. However, the intensity of absorption can be enhanced either by carrying NMR at low temperatures and/or by employing high magnetic field. Both these factors help in increasing the population difference between the two levels in accordance with the Boltzmann distribution law (Eq. 4.2.19).

The expressions of magnetic moment and its z-component are

$$\mu_m = g\mu_N \sqrt{I(I+1)} \quad (\text{Eq. 4.2.6})$$

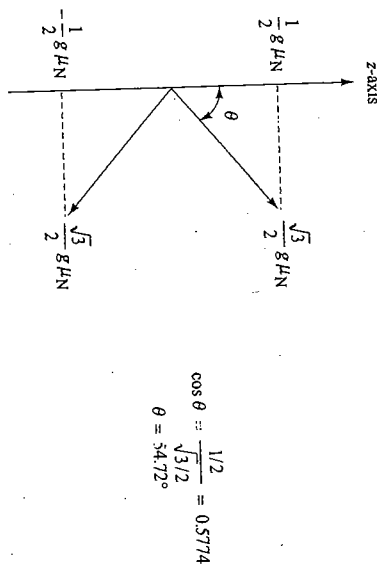
$$\mu_z = g\mu_N m_I \quad (\text{Eq. 4.2.11})$$

where  $I$  is the spin quantum number and  $m_I$  is the component spin quantum number. The permitted values of  $m_I$  are  $I, I-1, \dots, -(I-1), -I$ .

Since  $m_I$  can never be equal to  $\sqrt{I(I+1)}$ , it follows from Eq. (4.2.11) that  $\mu_z$  can never be equal to  $\mu_m$ , i.e. the magnitude of the magnetic moment vector and its z-component can never be the same. This means that the magnetic moment vector can never be directed along the magnetic axis and will always be oriented with respect to z-axis. The angle of orientation is given by

$$\cos \theta = \frac{\mu_z}{\mu_m} = \frac{m_I}{\sqrt{I(I+1)}} \quad (4.2.20)$$

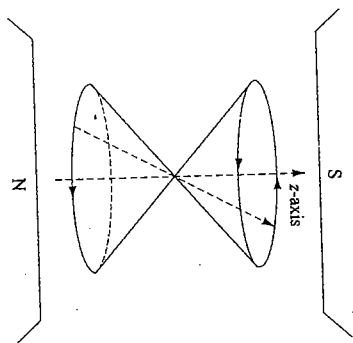
Fig. 4.2.2 The two orientations of magnetic moment vectors of a proton along the z-axis



For protons, the two directions of magnetic moment vector are shown in Fig. 4.2.2.

### Larmor Precession

In the presence of a magnetic field, the magnetic moment experiences a couple force which tends to align the vector along the field direction. This, however, is not possible because of the above quantum mechanical restriction. The only other effect of this force is to rotate the magnetic moment vector around the field direction keeping all the while its orientation angle  $\theta$  constant, i.e. the magnetic moment starts precessing around the magnetic field as shown in Fig. 4.2.3. This precession is known as the *Larmor precession*.



The Larmor frequency in radians per second is given by

$$\begin{aligned} \omega &= \gamma B = \left( \frac{2\pi \mu_N g}{h} \right) B \\ &= \frac{g \mu_N \sqrt{I(I+1)}}{h} B = \left( \frac{\text{Magnetic moment}}{\text{Angular momentum}} \right) B \end{aligned} \quad (4.2.21)$$

Equation (4.2.21) is identical with Eq. (4.2.18) implying that the Larmor frequency is equal to the angular frequency separation between the two nuclear magnetic energy levels.



The precession of magnetic moment means that the nuclear magnetic field is rotating around the external magnetic field. The potential energy of the nucleus remains constant in this precession. This potential energy can be changed by changing the orientation angle of the magnetic moment vector to the other permitted angle. This can be achieved by applying a secondary magnetic field rotating around the main field with a frequency equal to that of the precessing nucleus. Under this condition, the rotating magnetic field is in resonance with the precessing nuclear magnetic field and thus induces the transition from one level to the other level, giving rise to either absorption or emission of energy.

### Experimental Set Up

In NMR spectrometers, the rotating secondary magnetic field is produced by sending the output of a radiofrequency oscillator through a helical coil (solenoid) of wire whose axis is perpendicular to the direction of the main magnetic field. The latter is generated with the help of an electromagnet. The sample under study is placed in a glass tube positioned along the axis of the coil. An electric current passing through such a coil produces magnetic field in its centre and directed along the axis. This magnetic field reverses its direction with the same frequency as the current from the oscillator. This alternating magnetic field is equivalent to two rotating magnetic fields which are rotating in opposite directions with the same frequency (Fig. 4.2.4). One of these directions is the same as that of the precessional motion of the nucleus and this rotating field acts as a secondary magnetic field. When the frequency of the alternating current supplied to the coil and the magnetic field experienced by the nucleus have values equal to the frequency of separation between the two levels, a condition of resonance exists and thereby the nucleus can either absorb or emit energy from the secondary magnetic field. As stated earlier, there will be a net absorption of energy as the ground level is more populated than the excited level.

The above resonance phenomenon can be achieved by either of the following ways:

1. By varying the frequency of the oscillator keeping the external magnetic field constant.
2. By varying the external magnetic field keeping the frequency of the oscillator constant.

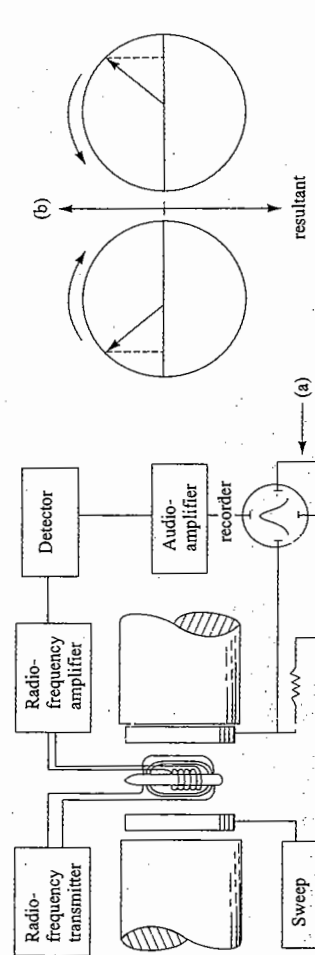


Fig. 4.2.4 (a) Experimental set up for NMR, and (b) generation of the rotating magnetic field

In the former, we are keeping the Larmor frequency at a constant value and varying the external circulating magnetic field till it becomes equal to the Larmor precessional frequency. However, in the latter, we keep the frequency of the external circulating magnetic field constant and vary the Larmor frequency till it becomes equal to the frequency of the external circulating magnetic field. In actual practice, it is preferable for most instruments to use a fixed frequency (usually 60 MHz) supplied by a crystal-controlled oscillator and to vary the magnetic field applied to the sample by an electromagnet.

What magnetic field strength is required for proton magnetic resonance at 220 MHz. Given: The factor  $g$  for proton is 5.585.

Since  $\Delta V = \mu_N g B$ , we have

$$B = \frac{\Delta V}{\mu_N g} = \frac{(220 \times 10^6 \text{ s}^{-1})(6.626 \times 10^{-34} \text{ J s})}{(5.047 \times 10^{-27} \text{ J T}^{-1})(5.585)} = 5.171 \text{ T}$$

Calculate the precessional frequency of a proton in a field of 1.5 T.

The precessional frequency is

$$\nu = \frac{\mu_N g B}{h} = \frac{(5.047 \times 10^{-27} \text{ J T}^{-1})(5.585)(1.5 \text{ T})}{(6.626 \times 10^{-34} \text{ J s})} = 6.38 \times 10^7 \text{ s}^{-1}$$

Calculate the value of gyromagnetic ratio  $\gamma$ .

The value of gyromagnetic ratio is

$$\gamma = \frac{2\pi \mu_N g}{h} = \frac{2(3.14)(5.047 \times 10^{-27} \text{ J T}^{-1})(5.584)}{(6.626 \times 10^{-34} \text{ J s})} = 2.671 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$$

Calculate the angular momentum and magnetic moment values for a proton. Given:  $g = 5.585$ .

We have

$$L = \sqrt{I(I+1)} \left( \frac{h}{2\pi} \right) \quad \text{and} \quad \mu_m = g \mu_N \sqrt{I(I+1)}$$

For a proton,  $I = 1/2$ . Thus, we have

$$L = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} \left( \frac{h}{2\pi} \right) = 0.866 \left( \frac{h}{2\pi} \right) = 0.866 \left( \frac{6.626 \times 10^{-34} \text{ J s}}{2 \times 3.14} \right) = 0.9137 \times 10^{-34} \text{ J s}$$

$$\text{and} \quad \mu_m = (5.585) (\mu_N) \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} = 4.837 \mu_N = 4.837 (5.047 \times 10^{-27} \text{ J T}^{-1}) = 2.441 \times 10^{-26} \text{ J T}^{-1}$$

## PMR of Organic Compounds

The NMR signal of a nucleus is highly characteristic of the nucleus under study. Moreover, the area under the NMR signal is directly proportional to the number of such resonating nuclei. Thus, NMR technique has been widely employed in determining the nature and number of resonating nuclei. The widest application of NMR is in the field of organic chemistry where it has been employed for the structural elucidation of organic compounds. It is a great blessing that  $^{12}\text{C}$  and  $^{16}\text{O}$  are the magnetic inactive atoms and thus do not exhibit any NMR signals. The only widest distributed magnetic active nucleus in organic compounds is the hydrogen atom, and hereafter, we shall focus attention only on the PMR spectroscopy.

The structure elucidation of organic compounds is based on two principles. These are the *chemical shift* and the *spin-spin interaction*.

### THE CHEMICAL SHIFT

The variation of potential energy of an isolated proton in the magnetic field has been shown in Fig. 4.2.1. However, while dealing with atoms or molecules, the various nuclei are not present as the bare nuclei but are associated with the electronic clouds. The density of electronic cloud around any particular nucleus in a molecule depends on its environment. In the presence of a magnetic field, the electronic cloud associated with any particular nucleus tends to circulate around the nucleus in a plane perpendicular to the applied field. This circulation, also known as *diamagnetic circulation*, produces an induced magnetic field which acts in the opposite direction of the external magnetic field. Thus, the effective field observed by a nucleus is not equal to the external magnetic field but a little less by an amount equal to the induced magnetic field, i.e.

$$B_{\text{observed}} = B_{\text{applied}} - B_{\text{induced}} \quad (4.2.22)$$

Now the induced magnetic field is directly proportional to the applied field, i.e.

$$B_{\text{induced}} \propto B_{\text{applied}}$$

$$\text{or} \quad B_{\text{induced}} = \sigma B_{\text{applied}} \quad (4.2.23)$$

where  $\sigma$  is a constant, called the *shielding constant*. Its value depends on the electron density around the nucleus in a molecule. If the electron density around any particular nucleus is larger than the other, it has a larger value of  $\sigma$  and is known to be more shielded with respect to the applied field. From Eq. (4.2.23), it follows that the nucleus with larger value of shielding constant will observe a larger opposite induced magnetic field and hence the actual field seen by such a nucleus will be smaller than that seen by a less shielded nucleus (Eq. 4.2.22).

Substituting Eq. (4.2.23) in Eq. (4.2.22), we get

$$B_{\text{observed}} = B_{\text{applied}} (1 - \sigma) \quad (4.2.24)$$

<sup>†</sup> See Annexure at the end of the chapter for the qualitative quantum mechanical study of NMR signals for simple molecules.

## PMR Spectrum of $\text{CH}_3\text{OH}$

For a bare proton,  $\sigma = 0$  and hence

$$B_{\text{observed}} = B_{\text{applied}}$$

For a proton in a molecule,  $\sigma$  is positive and hence

$$B_{\text{observed}} < B_{\text{applied}}$$

The extent of shielding will be constant for a given atom in isolation, but will vary in a molecule because of different chemical environments. Consider, for an example, the molecule  $\text{CH}_3\text{OH}$ . It has three identical C—H bonds and one O—H bond. The chemical environments of hydrogen atoms in C—H bonds and O—H bond are different. Since oxygen is more electronegative than carbon, the electron density on H in O—H bond will be less than that on H in the C—H bond. In other words, we can say that the hydrogen atom in C—H bond is more shielded than the hydrogen atom in the O—H bond, i.e.

$$\sigma_{\text{CH}} > \sigma_{\text{OH}}$$

Thus, from Eq. (4.2.24) it follows that

$$B_{\text{applied}} (1 - \sigma_{\text{CH}}) < B_{\text{applied}} (1 - \sigma_{\text{OH}})$$

$$\text{or} \quad (B_{\text{observed}})_{\text{CH}} < (B_{\text{observed}})_{\text{OH}}$$

that is, the actual field seen by the methyl protons will be lesser than that seen by the hydroxyl proton.

The spacing between the two nuclear levels in the presence of a magnetic field as given by Eq. (4.2.14) is

$$\Delta V = V_{-1/2} - V_{1/2} = g \mu_N B_{\text{observed}} = \gamma \frac{h}{2\pi} B_{\text{observed}}$$

$$= \gamma \frac{h}{2\pi} (1 - \sigma) B_{\text{applied}} \quad (4.2.25)$$

Since

$$(B_{\text{observed}})_{\text{OH}} > (B_{\text{observed}})_{\text{CH}} \quad (4.2.26)$$

it follows that for a given applied field, the energy levels of O—H protons will be more widely spaced than those of C—H protons. The effect of a steadily increasing magnetic field on the energy levels of —CH<sub>3</sub> and —OH protons are shown in Fig. 4.2.5.

Since most of NMR spectrometers are operated by using a constant frequency oscillator (usually at 60 MHz) and varying the external magnetic field, it is obvious from Fig. 4.2.5 that the hydroxyl proton will be thrown into resonance earlier than the methyl protons as the external magnetic field is steadily increased. This means that the PMR signal of hydroxyl proton will be observed at the low-end field and that of methyl protons at the high-end field (Fig. 4.2.5). The area under the signal



of methyl protons will be three times larger than that under the hydroxyl proton since in the former we have three identical protons. It may be recalled that neither oxygen nor carbon will exhibit any absorption as both of these are magnetic inactive nuclei.

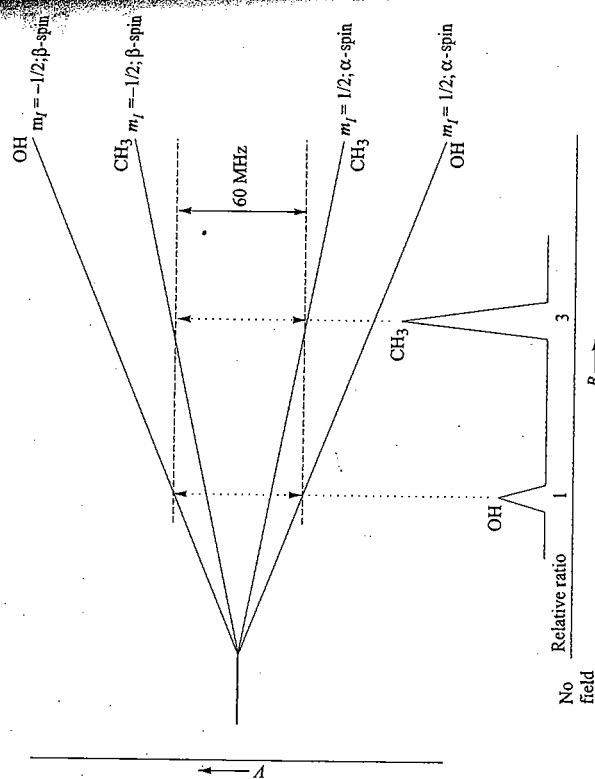


Fig. 4.2.5 Variation of potential energy of methyl and hydroxyl protons of  $\text{CH}_3\text{OH}$  in the presence of varying external magnetic field

### PMR Spectrum of $\text{CH}_3\text{CH}_2\text{OH}$

In ethyl alcohol, we have three different types of protons: (1) the hydroxyl proton, (2) the methylene protons, and (3) the methyl protons. Of these, the hydroxyl proton is expected to be the least shielded as it is attached to the more electronegative oxygen atom. Consequently, this proton will come into resonance at a field lower than those of methylene and methyl protons. Of the methylene and methyl groups, the hydrogen atoms attached to the former are expected to be less shielded as the  $\text{CH}_2$  group is directly attached to the oxygen atom. Thus, the methylene protons will come into resonance earlier than those of the methyl protons. The expected spectrum of ethyl alcohol is shown in Fig. 4.2.6. It has three absorption signals. The signal at the low-end field is due to the hydroxyl proton, at the high-end field is due to the methyl protons and at the centre is due to the methylene protons. The area under these peaks will follow the ratio 1 : 2 : 3 as they represent one proton of the OH group, two protons of the  $\text{CH}_2$  group and three protons of the  $\text{CH}_3$  group, respectively.

The spectrum shown in Fig. 4.2.6, which shows only the effects of chemical shift, is known as the *low-resolution spectrum*.

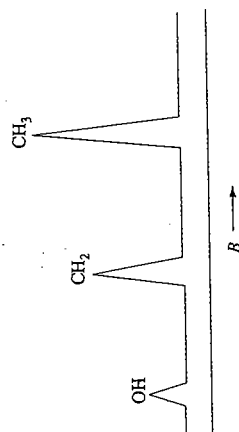


Fig. 4.2.6 Low-resolution spectrum of ethyl alcohol

### Expressing Chemical Shift

The spacing between the two signals of the same type of nuclei (say protons under different chemical environments) is known as the chemical shift. The numerical values of chemical shifts are very small as compared to the external applied magnetic field since  $B_{\text{induced}}$  is much smaller than  $B_{\text{applied}}$ . The magnitude of chemical shift is of the order of a few microtesla in a field of 1 T. Though the spectrum is recorded at constant radiation frequency and by varying the external magnetic field, yet in most cases, the chemical shifts are reported in the units of hertz as if the spectrum has been recorded by varying the applied frequency at a constant magnetic field. Both these scales are interrelated by the expression

$$\Delta V = \frac{\Delta E}{h} = \frac{g \mu_N}{h} \Delta B \quad (4.2.27)$$

The conversion factor is as follows.

$$\begin{aligned} \Delta V &= \frac{(5.585)(5.047 \times 10^{-27} \text{ J T}^{-1})}{(6.626 \times 10^{-34} \text{ J s})} (\Delta B) \\ &= (42.54 \times 10^6 \text{ T}^{-1} \text{ s}^{-1}) (\Delta B) \end{aligned}$$

If  $\Delta B$  is 1  $\mu\text{T}$ , i.e.  $10^{-6} \text{ T}$ , we have

$$\Delta V = 42.54 \text{ s}^{-1}$$

Thus, 1 microtesla  $\approx 42.54 \text{ s}^{-1}$

If  $\sigma_1$  and  $\sigma_2$  are the shielding constants of two protons under different chemical environments, then the chemical shift between them as given by Eq. (4.2.27) becomes

$$\begin{aligned} \Delta V &= \frac{\Delta E}{h} = \frac{g \mu_N}{h} (B_2 - B_1) \\ &= \frac{g \mu_N}{h} \{ B_{\text{applied}} (1 - \sigma_2) - B_{\text{applied}} (1 - \sigma_1) \} \\ &= \frac{g \mu_N}{h} B_{\text{applied}} (\sigma_1 - \sigma_2) \end{aligned} \quad (4.2.28)$$

Since  $\sigma$ s are independent of the applied field (or frequency of the oscillator), it is obvious from Eq. (4.2.28) that the chemical shift varies linearly with the external magnetic field (or frequency of the oscillator) and thus depends on the experimental conditions. However, this dependency can be removed if the chemical shift is reported as the fraction of the applied magnetic field (or the frequency). This

quantity, which is dimensionless, is multiplied by a factor of  $10^6$  to express it as parts per million (ppm). Thus, we have

$$\delta = \frac{B_{\text{ref}} - B_{\text{sample}}}{B_{\text{ref}}} \times 10^6 \quad (4.2.29)$$

where  $B_{\text{ref}}$  and  $B_{\text{sample}}$  are the values of the external magnetic field at which resonances occur of the protons of the reference compound and that of the given compound, respectively.<sup>†</sup>

The reference compound is dissolved in the same solution as the sample so that both are under the influence of the same external magnetic field. The reference compound which is universally selected for hydrogen resonances in non-aqueous solvents is tetramethylsilane ( $\text{CH}_3)_4\text{Si}$  or TMS in short. It has the following characteristics:

- It gives a single intense peak, since all the twelve hydrogen nuclei are equivalent.
- The hydrogen nuclei in TMS are highly shielded as compared to those in the organic compounds and hence exhibit resonance at a very high-field strength (1.409 2 T for 60 MHz radiation) which can easily be recognized.

- It has a low boiling point ( $27^\circ\text{C}$ ) and hence can be readily removed after the spectrum has been recorded.

In view of the limited solubility of TMS in water, the salt  $(\text{CH}_3)_3\text{SiCD}_2\text{CD}_2\text{CO}_2^-$  is commonly used in the solvent.

Two scales are commonly employed to represent the various signals. These are: (i) the  $\delta$ -scale, and (ii) the  $\tau$ -scale. On the  $\delta$ -scale,  $\delta$  is set equal to zero at the reference peak of TMS and it increases downfield. The only disadvantage of this scale is that a larger value of  $\delta$  implies a low-field resonance and hence a low shielding of the nucleus with respect to the external magnetic field. This disadvantage is removed in the  $\tau$ -scale where TMS signal is assigned a value of 10 and it decreases downfield. Thus, a low value of  $\tau$  means that the nucleus is less shielded and a higher value means the nucleus is more shielded. The two scales are related to each other by the expression

$$\tau = 10 - \delta$$

For most organic compounds, the  $\tau$ -value lies between 0 and 10 and is highly characteristic of the chemical environment. It is for this reason, they can be used to detect the type of proton that is present in a given organic molecule. Table 4.2.1 records some of the  $\tau$ -values of protons under different chemical environments.

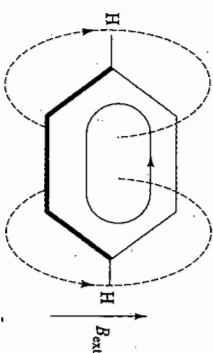
<sup>†</sup> Alternatively, in terms of frequency, we have

$$\delta = \frac{\Delta\nu}{\text{Fixed frequency of the probe}} \times 10^6$$

## Reference Compound in PMR Spectra

### Comment

Fig. 4.2.7 Ring current due to the circulation of  $\pi$  electrons

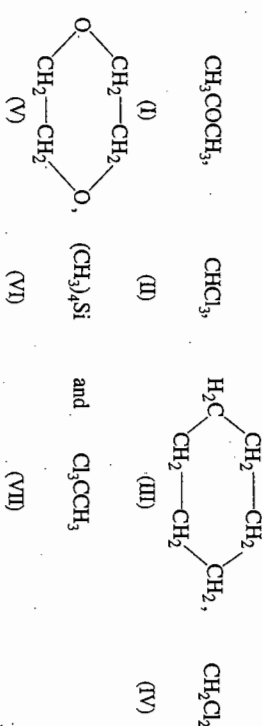


The PMR signal of benzene protons appears at lower field ( $\tau \approx 2.73$ ) as compared to those of aliphatic protons. This is attributed to the circulating current in benzene due to the six  $\pi$  electrons (Fig. 4.2.7). This produces a magnetic field at the sites of protons acting in the same direction of the external magnetic field. This results into larger deshielding of protons, hence, exhibits the signal at the low-end magnetic field.

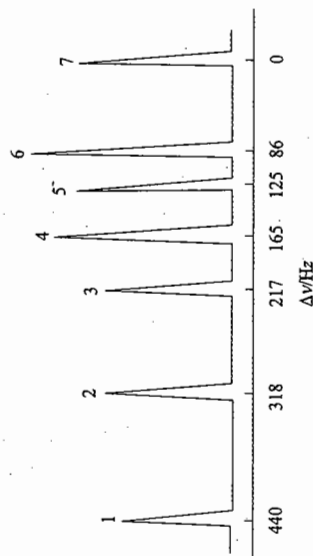
Table 4.2.1  $\tau$ -Values of Hydrogens in Some of the Organic Compounds

Compound	$\tau$ -value	Compound	$\tau$ -value
Tetramethylsilane	10	Methyl alcohol	6.62
Cyclopropane	9.78	Methyl protons	6.2
Methane	9.77	Dioxane	5.72
Tetramethylmethane	9.08	Nitromethane	4.8
Ethyl alcohol	8.83	Water	4.2
Methyl protons	6.41	Methylene chloride	4.16
Cyclohexane	8.56	Ethylene	2.73
Methyl cyanide	8.03	Benzene	2.3
Acetone	7.91	Chloroform	2.27
Acetaldehyde	7.85	Naphthalene	1.6
Methyl protons	0.28	Sulphuric acid	
Aldehydic proton			

Figure displays a PMR-spectrum (without the intensity factor) at 60 MHz of a solution containing the following components in deuteriochloroform.



(a) Match each of the components with the corresponding peak (say, for example, the peak 7 represents the compound VI).



Effect of a Neighbouring Proton

- (b) What would be the position (in Hz) of the chloroform peak at 60 MHz with reference to the cyclohexane peak?
- (c) Express the separation of each line with reference to TMS line in each of the three scales (Hz,  $\delta$ - and  $\tau$ -scales). What would be the separation of these peaks at 100 MHz? Give the answer in each of three scales.
- (a) The position of absorption of a proton depends on its electronic environment. A less shielded proton shows the signal at the low-end field and the more shielded at the high-end field. All protons of a molecule in the above list of molecules are identical and hence will exhibit only one absorption. The shielding constants of protons in given molecules are expected to follow the following order:



Thus, the assignment of peaks is as follows.

Molecule	VI	III	I	V	VII	IV	II
Peak	7	6	5	4	3	2	1

- (b) Chloroform peak is at 440 Hz and that of cyclohexane is at 86 Hz. Thus, chloroform peak lies 354 Hz (= 440 Hz - 86 Hz) away from the cyclohexane peak towards the low-end field.

- (c) The separation of each line with reference to TMS line in terms of Hz,  $\delta$ - and  $\tau$ -scales are described below.

Molecule	Hz	$\delta$ -value	$\tau$ -value
TMS	0	0	10
Cyclohexane	86	86/60 = 1.43	8.57
Acetone	125	125/60 = 2.08	7.92
Dioxane	165	165/60 = 2.75	7.25
1-1-1 Trichloroethane	217	217/60 = 3.61	6.39
Dichloromethane	318	318/60 = 5.30	4.70
Trichloromethane	440	440/60 = 7.33	2.67

## THE SPIN-SPIN INTERACTIONS

The actual field observed by a proton, besides depending on the surrounding electron density, is also influenced by the neighbouring magnetic active nuclei. This is due to the spin-spin interactions. A proton can have either  $\alpha$ -spin ( $m_I = +1/2$ ) or  $\beta$ -spin ( $m_I = -1/2$ ). These spins are represented by arrows;  $\alpha$ -spin is represented by an arrow pointing upwards and  $\beta$ -spin by an arrow pointing downwards. Consider a situation in which the proton A is present in the neighbourhood of the other proton B. The field observed by the proton A will be dependent upon the spin of the proton B, and vice versa. We can consider the following two alternatives:

- (i) *Proton B has  $\alpha$ -spin* When the proton B has  $\alpha$ -spin, then it creates a magnetic field on A which acts in the opposite direction of the external magnetic field (Fig. 4.2.8). Thus, the actual field observed by the proton A is

$$B_{\text{observed}} = B_{\text{applied}} - B_{\text{interaction}} \quad (4.2.30)$$

where  $B_{\text{interaction}}$  is the field generated by the proton B on the proton A.

- (ii) *Proton B has  $\beta$ -spin* When the proton B has  $\beta$ -spin, it creates a magnetic field on the proton A which acts in the same direction as that of the external magnetic field (Fig. 4.2.8). Thus, the actual field seen by the proton A is

$$B_{\text{observed}} = B_{\text{applied}} + B_{\text{interaction}} \quad (4.2.31)$$

where  $B_{\text{interaction}}$  is the field generated by the proton B on the proton A.

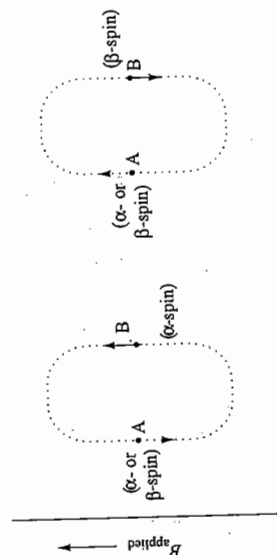


Fig. 4.2.8 The spin-spin coupling between the two protons

## Effect on Potential Energy

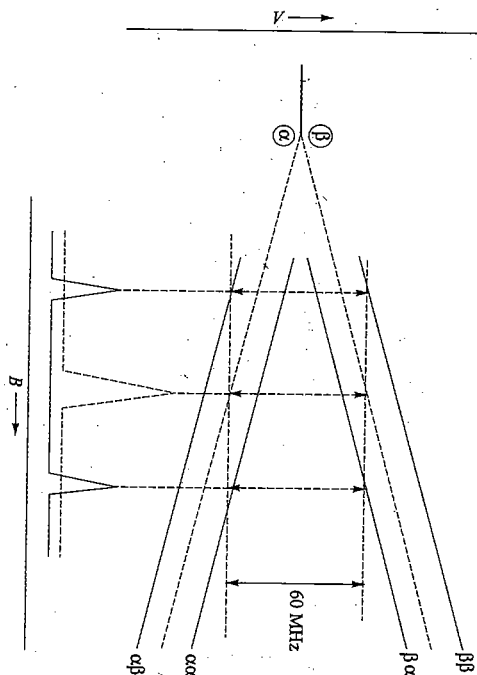
The potential energy of proton A will now be given by the relations

$$V_{\alpha} = -\mu_N g (B_{\text{applied}} - B_{\text{interaction}}) m_I$$

$$\text{and } V_{\beta} = -\mu_N g (B_{\text{applied}} + B_{\text{interaction}}) m_I$$

where the subscripts  $\alpha$  and  $\beta$  represent, respectively, the spins  $\alpha$  and  $\beta$  of the neighbouring proton B. The variation in potential energy with the external magnetic field is shown in Fig. 4.2.9.

Fig. 4.2.9 Variation of potential energy of a proton in the presence and absence of a neighbouring proton. The levels  $\alpha\alpha$  and  $\beta\beta$  are destabilized and those  $\alpha\beta$  and  $\beta\alpha$  are stabilized



### PMR Spectrum

If the system is irradiated with a radiation of 60 MHz (or of any other frequency), then it can be concluded from Fig. 4.2.9 that the single absorption which is expected to occur in the absence of spin-spin interaction (shown by broken line) splits into two symmetrically placed absorptions, one with  $\alpha$ -spin of the neighbouring proton and the other  $\beta$ -spin of the neighbouring proton (shown by solid line).<sup>†</sup> The absorption corresponding to the  $\alpha$ -spin of the neighbouring proton lies towards the high-end field whereas that of the  $\beta$ -spin towards the low-end field. The area under these two peaks will be identical to that under the one peak observed in the absence of spin-spin coupling. The spin-spin splitting separation between the component lines usually has a small value as compared to the chemical shift of the involved protons and can be observed only if the spectrometers of high resolution are employed. This implies that the variation in the magnetic field should be recorded with the minimum precision of one part in  $10^7$ . It is for this reason, the recorded spectrum is known as the *high-resolution spectrum*.

The spin-spin interaction decreases very rapidly as the distance between the protons is increased and this interaction is transmitted through the bonds. In molecules, it operates only between the next nearest neighbours. Moreover, the interaction is always mutual, i.e. if the splitting of A occurs due to the interaction of the neighbouring proton B, then there will also occur the splitting of the signal of B. It is an *intramolecular* behaviour, i.e. the PMR signals of one molecule will not be affected by the protons of the other molecule. The spin-spin splitting separation between the component lines is also found to be independent of the external magnetic field.

In organic molecules, the spin-spin interaction may involve more than one neighbouring proton. Take, for example, the methyl alcohol in which the hydroxyl proton interacts with the three identical protons of methyl group. We consider now the scheme for this type of interactions. We restrict ourselves to the simple type

<sup>†</sup> During the transition, the spin of neighbouring proton does not change. This is, in fact, the selection rule for the nuclear spin transitions.

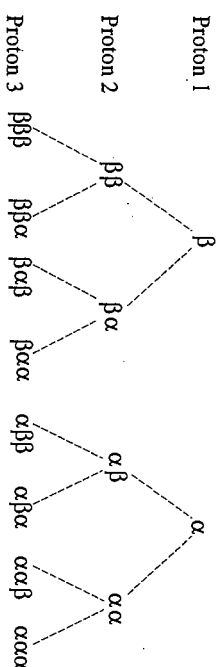
### High-Resolution Spectrum of Methyl Alcohol

of molecules in which the chemical shift between the involved protons is much larger than the coupling constant (the separation between the two splitted lines of the same signal). Such types of molecules are abbreviated as  $A_nX_m$ , where A and X represent the two different neighbouring protons in a molecule. We discuss below the scheme of spin-spin interactions with the typical examples of methyl alcohol and ethyl alcohol.

The three hydrogen atoms of methyl group have the same chemical environment and thus have the same shielding constant. Consequently, the chemical shifts of all the three hydrogen atoms are identical. The rotation of methyl group around the C—O bond makes all the three protons of methyl group magnetically equivalent to the hydroxyl proton, and thus the interactions of methyl protons with the hydroxyl proton are all equal. It is known that the couplings within a group of magnetically and chemically equivalent nuclei do not affect the spectrum and can be ignored. Thus in methyl alcohol, we need not consider the couplings amongst the protons of methyl group and should consider only the coupling of methyl protons with the hydroxyl proton and vice versa (see Annexure at the end of the chapter). These are considered below:

**Coupling of methyl protons with the hydroxyl proton** The methyl protons will observe two possible arrangements of the hydroxyl proton, viz.,  $\alpha$  and  $\beta$ , and hence the field observed by methyl protons is modified in two different ways. Remembering that the field generated by  $\alpha$ -spin acts in the opposite direction and that generated by  $\beta$ -spin in the same direction of the external magnetic field, we may conclude that the actual field observed by methyl protons will be slightly greater than the external field when the hydroxyl proton has  $\beta$ -spin and it will be slightly less when the hydroxyl proton has  $\alpha$ -spin. Accordingly, the variation of potential energy of methyl protons will be represented by two lines; one corresponding to the field ( $B_{\text{applied}} - B_{\text{interaction}}$ ) and the other to the field ( $B_{\text{applied}} + B_{\text{interaction}}$ ). These are shown in Fig. 4.2.10.

**Coupling of hydroxyl proton with methyl protons** The hydroxyl proton couples with the neighbouring three methyl protons. Each proton can have either  $\alpha$ -spin or  $\beta$ -spin. The total number of possible arrangements which the hydroxyl proton observes when each proton of methyl group has either  $\alpha$ -spin or  $\beta$ -spin are as follows.



There are eight arrangements in all. These fall into the following categories:

1. All the three protons have  $\alpha$ -spins.
2. Two of them have  $\alpha$ -spin and the third has  $\beta$ -spin.
3. Two of them have  $\beta$ -spins and the third has  $\alpha$ -spin.
4. All the three protons have  $\beta$ -spins.

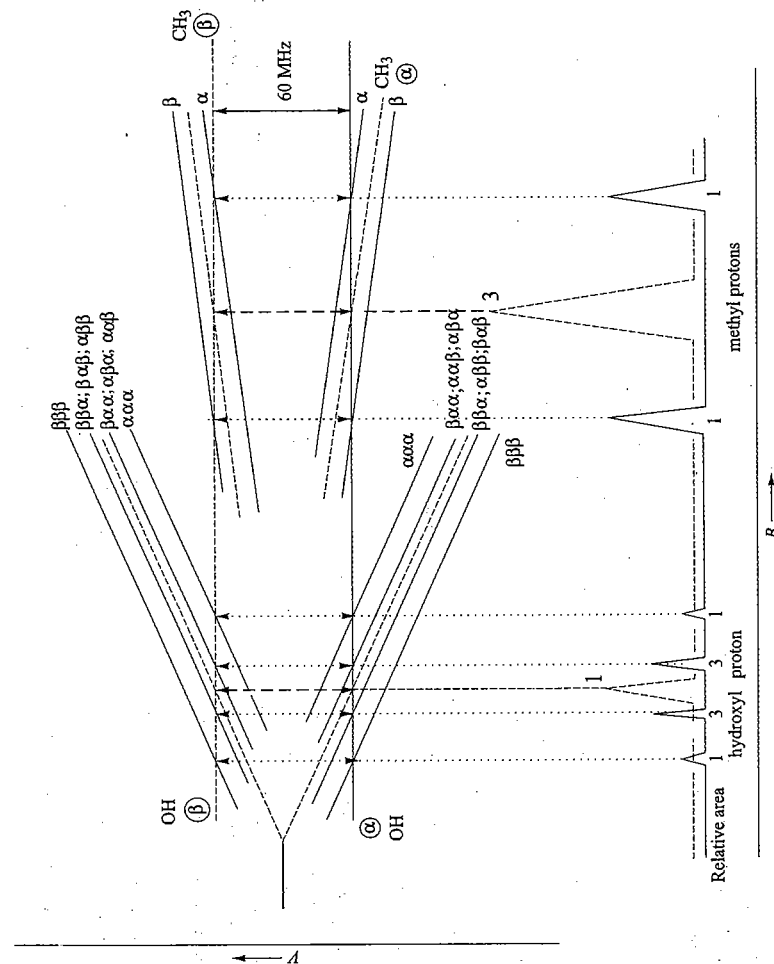


Fig. 4.2.10 High-resolution spectrum of methyl alcohol

The number of such combinations in each of the above four categories are 1, 3, 3, 1, respectively. It means that the number of hydroxyl protons observing either 2α and 1β or 2β and 1α arrangement of methyl protons will be three times larger than those observing either 3α or 3β arrangement. Each of these arrangements will affect the magnetic field on the hydroxyl proton. Remembering again that the α-spin generates the field in the opposite direction and that generated by β-spin is in the same direction as the external magnetic field, we may conclude that the field observed by the hydroxyl proton will follow the order given below.

$$(B_{\text{observed}})_{3\alpha} < (B_{\text{observed}})_{2\alpha \text{ and } 1\beta} < (B_{\text{observed}})_{\alpha\alpha \text{ and } \alpha\beta} \\ < (B_{\text{observed}})_{2\beta \text{ and } 1\alpha} < (B_{\text{observed}})_{3\beta}$$

where the subscripts represent the arrangements of the neighbouring methyl protons and the field  $(B_{\text{observed}})_{\alpha\alpha \text{ and } \alpha\beta}$  represents the field in the absence of spin-spin interaction. Thus, the variation of potential energy of the hydroxyl proton will be represented by four different lines corresponding to each of the four different arrangements of methyl protons. These are shown in Fig. 4.2.10.

Now if the system is irradiated with a radiation of 60 MHz, we find that two absorption lines are observed for methyl protons and four absorption lines for hydroxyl proton as shown at the foot of Fig. 4.2.10. The two absorption lines of methyl protons will have identical intensities whereas those of hydroxyl proton will have the intensity ratio of 1 : 3 : 3 : 1. The ratio 1 : 3 : 3 : 1 arises because of the fact that the number of arrangements of 2α and 1β, and 2β and 1α are three times larger than those of 3α and 3β. The total area under the two absorption lines of methyl protons will be identical to the corresponding single absorption observed in the absence of spin-spin coupling (shown by broken line). Similarly the area under the four peaks of hydroxyl proton will be identical to the corresponding single absorption in the absence of spin-spin coupling.

### Characteristics of High-Resolution Spectrum

In general, if a proton is coupled with the neighbouring  $n$  equivalent (magnetically and chemically) protons, the number of absorptions observed is  $(n + 1)$ . Their relative intensities are given by†

$${}^nC_m = \frac{n!}{m!(n-m)!}$$

where  $m$  goes from 0 to  $n$ . The above general rule will be applicable only in case of  $A_nX_m$  molecules where the chemical shift between the involved protons is much larger than the spin-spin coupling constant. If these two are comparable, complex patterns are obtained, which can, however, be analysed by the quantum mechanical method.

It may once again be recalled that the spin-spin couplings are intramolecular interactions and thus are independent of the external magnetic field. On the other hand, chemical shifts do depend on the external magnetic field. Thus, recording a spectrum at different magnetic fields merely changes the chemical shifts and not the spin-spin couplings. In general, recording a NMR spectrum at a very high frequency (say, 100 MHz) often simplifies the pattern that is observed at the low frequency (say, 40 MHz). This is due to the fact that at high frequency, the spin-

† An easy way to determine the relative intensities is to use Pascal's triangle, given by

$n$	relative intensities
0	1
1	1 1
2	1 2 1
3	1 3 3 1
4	1 4 6 4 1
5	1 5 10 10 5 1
6	1 6 15 20 15 6 1

where the coefficients in additional rows can be determined by adding the coefficients to the right and left of the desired coefficient in the previous row.

spin couplings, which are comparable with the chemical shifts at low frequency, become negligible in comparison to the latter. This arises because of the fact that the spin-spin couplings remain unaltered whereas the chemical shifts are magnified in proportion to the change in frequency of the radiation.

### General Remarks about Spin-Spin Coupling

In general, the chemically equivalent protons do not exhibit spin-spin splitting in the NMR spectrum in spite of the fact that there exist spin-spin interactions amongst them (See Annexure). Thus, only single proton resonance line is observed for the molecules  $H_2$ ,  $CH_4$ ,  $C_2H_6$ , etc. The effect of one proton on the resonance of another proton or group of equivalent protons depends on the number and kind of intervening chemical bonds. Normally, the splitting for nonequivalent protons in saturated molecules are of the order of 15 Hz when located on the same carbon, 5 to 8 Hz when located on the next neighbouring carbons and essentially zero when separated by more than two carbons.

### High-Resolution Spectrum of Ethyl Alcohol

The low-resolution spectrum of ethyl alcohol was described earlier. We get three peaks corresponding to one hydroxyl proton at the low-end field, three methyl protons at the high-end field and two methylene protons in between these two fields. In high-resolution spectrum, the absorption peak of methyl protons will split into three peaks with relative intensities as 1, 2, 1 since it is attached to the methylene group. The absorption peak of methylene protons will primarily split into four peaks with intensities 1, 3, 3, 1 due to the interaction with the methyl protons. Each of these four peaks will further split into two peaks of equal intensity due to the coupling with the hydroxyl proton. Thus, in a very high resolution spectrum, the methylene protons will exhibit an octet with relative intensities 1, 1, 3, 3, 3, 3, 1, 1. If the resolution is not very large, one often finds quintet with intensities 1, 4, 6, 4, 1, as if it has coupled with four protons (three from methyl and one from hydroxyl). The hydroxyl proton will split into three peaks of intensities 1, 2, 1 due to the coupling with methylene protons.

The expected high-resolution spectrum of ethyl alcohol is shown in Fig. 4.2.11a.

### Ethyl Alcohol Spectrum in the Presence of Trace of Acid or Alkali

The hydroxyl proton of ethyl alcohol is not immutably locked in any particular ethyl alcohol molecule. It is, in fact, being continuously exchanged from one molecule to the other molecule. The rate of this exchange is relatively slow in pure ethyl alcohol. The time spend by the proton on any ethyl alcohol molecule is quite sufficient to allow the interaction with the neighbouring methylene protons and thus causing spin-spin splitting. In the presence of acid or alkali, the rate of transfer of hydroxyl proton from one molecule to the other is very much enhanced and thus the time spend by the hydroxyl proton with any particular molecule is too small to allow the interaction with the methylene protons. Thus, the splitting of hydroxyl and methylene protons due to each other is completely prevented and thus one observes a single peak of the hydroxyl proton. Likewise, the methylene protons show only splitting due to the neighbouring methyl protons and hence the quintet is replaced by the quartet. The resultant spectrum is shown in Fig. 4.2.11b.

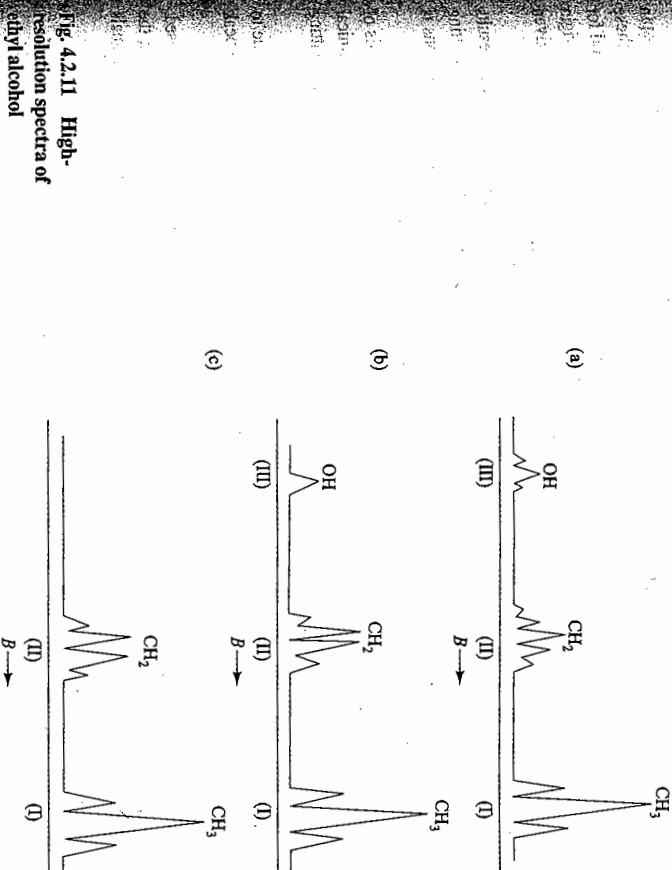
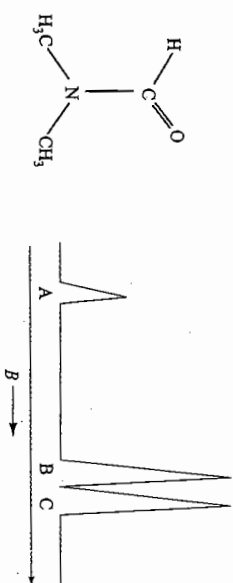


Fig. 4.2.11 High-resolution spectra of ethyl alcohol

### Ethyl Alcohol Spectrum in the Presence of $D_2O$

On adding  $D_2O$  in ethyl alcohol, the hydroxyl proton of the latter is replaced by deuterium nucleus. It is thus expected that under such conditions, the absorption peak of hydroxyl proton will disappear (Fig. 4.2.11c). Though deuterium nucleus is also magnetic active ( $I = 1$ ), no absorption peak corresponding to this is observed in the magnetic field range over which the spectrum is scanned. This is due to the fact that the NMR-frequency of deuterium nucleus occurs at a very small frequency as compared to the hydrogen nucleus; 9.21 MHz as compared to 60 MHz in a magnetic field of strength 1.4 T. In order that the peak corresponding to the deuterium nucleus may be observed, one has to employ a very large magnetic field of  $1.4 \times 60/9.1 (= 9.1)$  tesla if the frequency of radiation is kept at 60 MHz. Since the magnetic moment of deuterium is much smaller than proton, the spin-spin interactions of deuterium with neighbouring protons may be neglected.

The PMR spectrum of dimethylformamide at 40 MHz and at room temperature is shown in the following figure.



The doublet B, C might arise either from chemically different groups or from spin-spin coupling. (i) What feature of the spectrum immediately rules out one of these explanations in this case? (ii) What experimental operation offers a general method for distinguishing between chemical shift and spin-spin splitting? (iii) Explain the origin of the lines A, B and C. (iv) What will be the effect of temperature on the given spectrum?

### Solution

(i) The doublet B and C arise due to the chemically different methyl groups. This results because of the restricted rotation around C—N axis. The possibility of spin-spin splitting may be excluded since it is on the mutual basis, i.e. if the peak of methyl protons is split into two, the CH peak would have split into seven peaks.

(ii) The chemical shift and the spin-spin splitting can be distinguished on the basis of their behaviour when the molecule is placed in a changing magnetic field. The chemical shift changes in proportion to the change in the magnetic field whereas spin-spin splitting remains unchanged.

(iii) Peak A is due to the proton of CH group as it is least shielded. Peak B is due to the protons of methyl group near to the CO group (i.e. in the *cis* position) and the peak C is due to the *trans* methyl group.

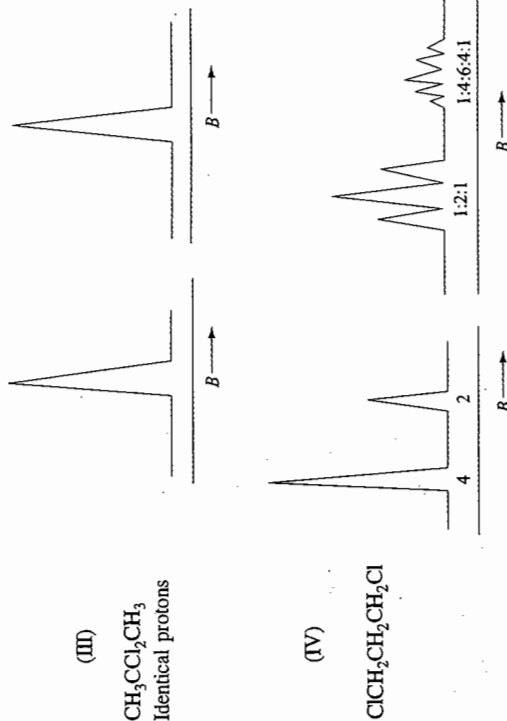
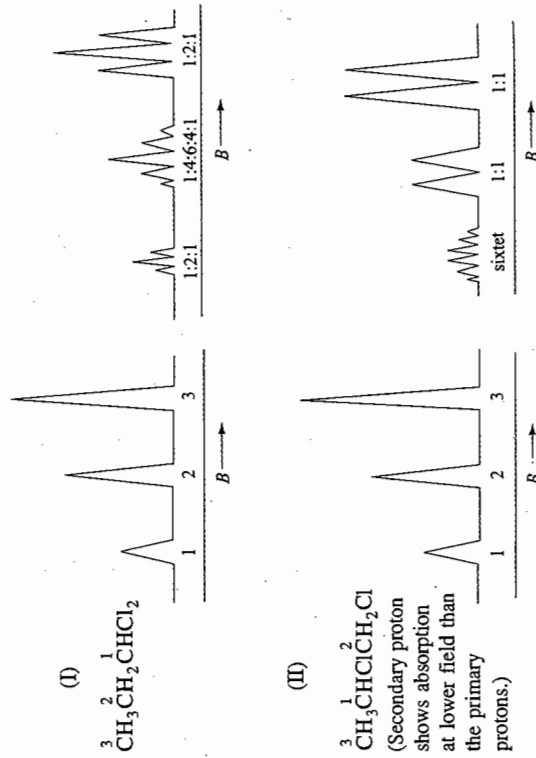
(iv) On increasing temperature, the restricted rotation around CN axis is decreased. At very high temperatures, the rotation speed becomes very large and hence both the methyl groups become identical. This will result in the collapse of the two given signals into a single peak.

### Problem 4.2.3

Write down all possible structural formulae having molecule formula  $C_3H_6Cl_2$ . Is it possible to identify them on the basis of low or/and high PMR spectra? Ignore the interactions of Cl atoms with H.

### Solution

The structural formulae of  $C_3H_6Cl_2$  along with their low and high resolution spectra are given below.



It may be concluded that the structural formulae are identifiable on the basis of low and high resolution spectra. The only exception is the identical low resolution spectra of compounds (I) and (II). However, they may be distinguished from the following points.

1. The  $\tau$ -value of the first peak of compound (I) is expected to be much lower than that of the first peak of compound (II), since the former represents a proton attached to the two chlorine atoms while the latter represents a proton attached to the one chlorine atom.

2. The chemical shift between the first and second peaks of compound (I) is expected to be larger than the corresponding chemical shift of compound (II).

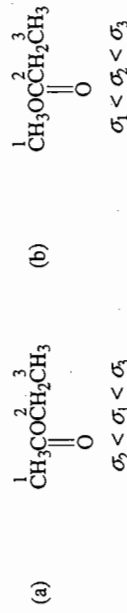
### Problem 4.2.4

Predict whether it is possible to distinguish the following two compounds on the basis of their low or/and high resolution PMR spectra.



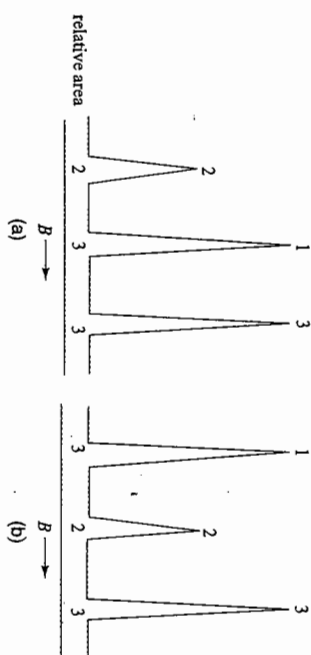
### Solution

Low-Resolution PMR Spectra The expected order of shielding constants of protons in the given compounds are



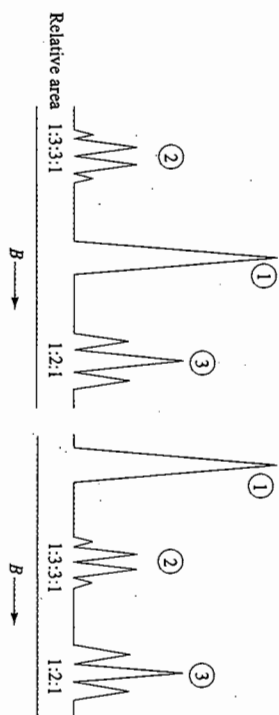
Thus, their low-resolution PMR spectra would look like as shown in the following figure.





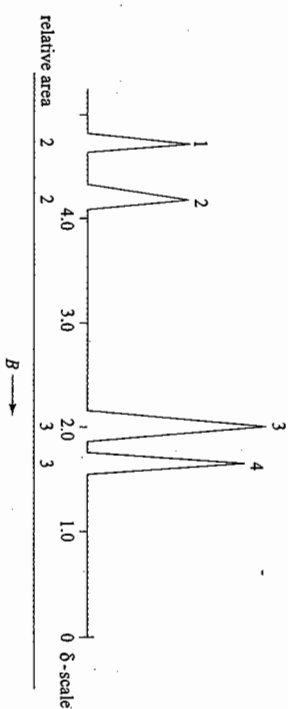
Since the two spectra are not identical, the two compounds are distinguishable from their low-resolution spectra.

**High-Resolution PMR Spectra:** Peak 2 in both the low-resolution spectra will split into four as the methylene group is attached to the methyl group. Similarly, peak 3 in both the spectra will split into three. Peak 1 will remain unaffected. Thus, the high-resolution PMR spectra would look like as shown in the following figure.



### Problem 4.2.5

Given in figure is the low-resolution PMR spectrum of  $C_6H_{10}O_2$ . Suggest its structure.



**Analysis of the spectrum**

- The relative areas of different peaks suggest the presence of two methylene groups (peaks 1 and 2) and two methyl groups (peaks 3 and 4).
- If we subtract two methylene and two methyl groups from  $C_6H_{10}O_2$ , we get  $C_2O_2$ . The latter may represent two CO groups.

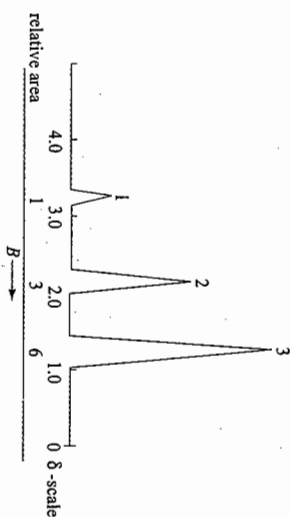
### Solution

The probable structure consistent with the above facts is



### Problem 4.2.6

Given in figure is the low-resolution spectrum of  $C_5H_{10}O_2$ . Suggest its structure.

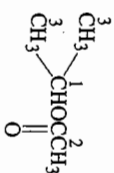


**Analysis of the spectrum**

The relative areas of different groups suggest that

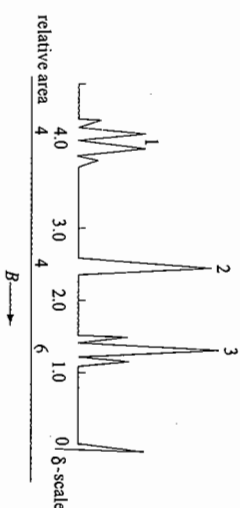
- Peak 1 must be due to a CH group. The latter must be attached with a stronger electron withdrawal group.
- Peak 2 must represent a methyl group.
- Peak 3 must represent two identical methyl groups. Protons of these methyl groups are more shielded than the protons of the other methyl group (peak 2).

If we subtract CH,  $CH_3$  and two  $CH_3$  groups from  $C_5H_{10}O_2$ , we get  $CO_2$  as the remaining fragment. We may conclude that the molecule is a derivative of a carboxylic acid. The two identical methyl groups and one CH group may arise from the isopropyl group. Since CH group shows peak at the high  $\delta$ -value, we may conclude that it is attached directly to the carboxylate group. The probable structure consistent with the above facts is



### Problem 4.2.7

Given figure is the PMR spectrum of  $C_8H_{16}O_4$ . Suggest its structure.



**Analysis of the spectrum**

- The hydrogen atoms represented by the peak 1 must be attached to a methyl group.
- The hydrogen atoms represented by the peak 3 must be attached to a methylene group.

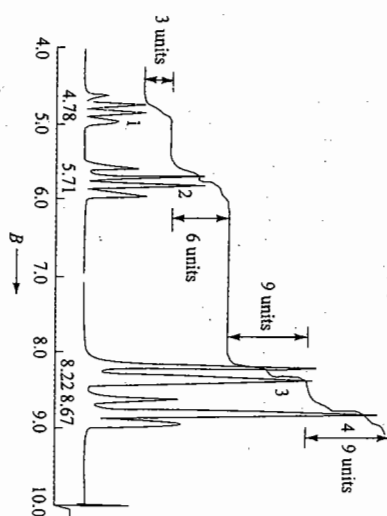
### Solution





**Problem 4.2.10**

Given in figure is the PMR spectrum of the compound  $C_5H_5O_4N$ . Suggest its structure.

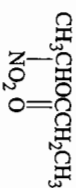
**Solution***Analysis of the spectrum*

1. The integral trace analysis indicates the presence of 1, 2, 3 and 3 protons in the peaks 1, 2, 3 and 4, respectively.
2. The peak 1 which represents one proton must be attached to a methyl group. This suggests the presence of  $-\text{CHCH}_3$  group.

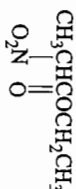
3. The quartet of peak 2 also indicates the coupling of two protons with the three protons. Thus, the presence of  $-\text{CH}_2\text{CH}_3$  group is indicated.

4. The points 2 and 3 discussed above account for all protons of the given molecule. The remaining fragment still to be accounted for is  $\text{CO}_2\text{N}$ . This may be present as  $-\text{C}(=\text{O})-\text{O}-$  and  $-\text{NO}_2$  groups.

Structures consistent with the above fragments are



(A)



(B)

However, the structure A may be ruled out on the basis that the expected  $\tau$ -value of CH group will be far away from that of  $\text{CH}_2$  group, since the former is attached the two strong electron withdrawing groups.

**4.3 ELECTRON SPIN RESONANCE SPECTROSCOPY**

Another spectroscopy which requires the use of radiation in the radiofrequency region of electromagnetic radiation is the electron spin resonance (ESR) or electron paramagnetic resonance (EPR). The theory of ESR is developed on the same line as that of PMR. In the latter, we deal with the interaction of a positively charged proton with the external magnetic field whereas in the former the interaction is

### Magnetic Characteristics Associated with Spin of Electron

between a negatively charged electron and the external magnetic field. We describe below, in brief, the theory of ESR.

The spinning of an electron is characterized by its spin quantum number which has a value of  $1/2$ . The magnitude of angular momentum is  $\sqrt{s(s+1)} (h/2\pi)$  (i.e.  $\sqrt{3}h/4\pi$ ). The  $z$ -component of the intrinsic angular momentum is  $m_s(h/2\pi)$ , where  $m_s$  has a value of either  $+1/2$  ( $\alpha$ -spin) or  $-1/2$  ( $\beta$ -spin). Thus, the angular momentum can have only two orientations in the presence of the magnetic field (Fig. 4.3.1). The orientation angle  $\theta$  is given by the relation

$$\left( \sqrt{s(s+1)} \frac{h}{2\pi} \right) \cos \theta = m_s \frac{h}{2\pi} \quad (4.3.1)$$

$$\text{or} \quad \sqrt{s(s+1)} \cos \theta = m_s \quad (4.3.2)$$

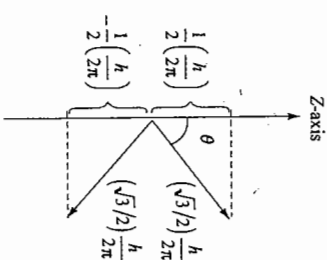


Fig. 4.3.1 The two orientations of spin angular momentum vector

The spinning of the electron around its own axis generates a magnetic dipole, the magnetic moment of which is given by

$$\begin{aligned} \mu_m &= -g \left( \frac{eh}{4\pi m_e} \right) \sqrt{s(s+1)} \\ &= -g \mu_B \sqrt{s(s+1)} \end{aligned} \quad (4.3.3)$$

where  $g$  is known as the *Lande splitting factor* and  $\mu_B$  is the basic unit of the magnetic moment for the electron, known as the *Bohr magneton*. The direction of the vector is that of the linear motion of a right-handed screw turned in the same sense as the current and pointing perpendicular to the plane of the coil. The unit of  $\mu_m$  in SI unit is  $\text{A m}^2$ .

The value of  $g$  for a free electron is found to be 2.0023. The value of  $\mu_B$  as calculated in Eq. (3.15.5) is

$$\mu_B = 9.2741 \times 10^{-24} \text{ J T}^{-1} \quad (4.3.4)$$

The negative sign in Eq. (4.3.3) indicates that the direction of the magnetic moment vector is opposite to that of the angular momentum as shown in Fig. 4.3.2.

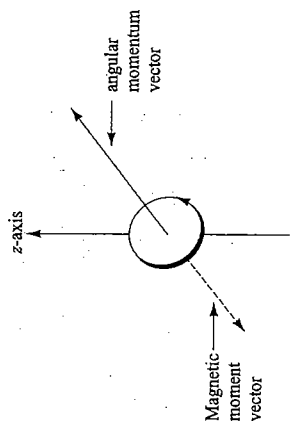


Fig. 4.3.2 The orientation of magnetic moment vector relative to that of angular momentum vector

### Potential Energy of Electron in a Magnetic Field

The potential energy  $V$  of an electron when placed in a magnetic field  $B$  is given by the expression

$$V = -B \mu_z = -B(\mu_m \cos \theta) \quad (4.3.5)$$

Substituting the expression of  $\mu_m$  from Eq. (4.3.3), we get

$$V = -B \left( -g \mu_B \sqrt{s(s+1)} \right) \cos \theta \\ = B g \mu_B m_s \quad (4.3.6)$$

Since  $m_s$  has only two values, we have

$$V_{+1/2} = (1/2) g \mu_B B ; \quad m_s = 1/2 \quad (4.3.7a)$$

$$V_{-1/2} = -(1/2) g \mu_B B ; \quad m_s = -1/2 \quad (4.3.7b)$$

### Variation of Potential Energy with Magnetic Field

The variations of  $V_{+1/2}$  and  $V_{-1/2}$  with magnetic field are shown in Fig. 4.3.3. The energy of  $\alpha$ -spin increases linearly whereas that of  $\beta$ -spin decreases with the increase in the external magnetic field. These variations can be rationalized by the direction of tiny magnet that is generated as a result of spinning of the electron. In  $\alpha$ -spin, the generated magnet has an unfavourable orientation, i.e. the north pole of the tiny magnet is nearer to the north pole of the external magnet, thus causing more and more repulsion as the external magnetic field is increased. In  $\beta$ -spin, the generated tiny magnet has a favourable direction so as to give rise to a net attraction.

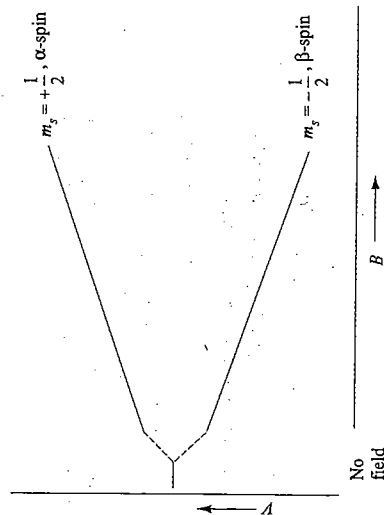


Fig. 4.3.3 The variation of potential energy of an electron in the presence of an external magnetic field

### Potential Energy Difference at a Given Magnetic Field

The difference in energy between the two levels of electron at a given magnetic field is

$$\Delta V = (1.854 \times 10^{-23} \text{ J T}^{-1}) B \\ \nu = \frac{(1.854 \times 10^{-23} \text{ J T}^{-1}) B}{(6.26 \times 10^{-34} \text{ J s})} = (2.86 \times 10^{10} \text{ s}^{-1} \text{ T}^{-1}) B$$

The strength of the applied magnetic field in most of ESR experiments is of the order of a few thousand gauss—say 3 000 gauss (i.e. 0.3 tesla). At this field strength, the energy difference is

$$\nu = (2.86 \times 10^{10} \text{ s}^{-1} \text{ T}^{-1}) (0.3 \text{ T}) = 8.58 \times 10^9 \text{ Hz}$$

which falls in the radiofrequency region of the electromagnetic spectrum ( $3 \times 10^6 - 3 \times 10^{10}$  Hz). On comparing the above energy difference between the two levels of an electron with that involved in the two levels of a proton in NMR spectroscopy, we find that the former is larger than the latter. The reason behind this is the smaller mass of the electron relative to that of a proton.

The relative distribution of electrons over the two levels as governed by the Boltzmann distribution law is

$$\frac{n_{1/2}}{n_{-1/2}} = \exp\left(-\frac{\Delta V}{kT}\right) \quad (4.3.8)$$

Thus, the lower level is more populated than the upper level. The difference of population in the present case will be larger than the population difference between the two PMR levels because of the larger value of  $\Delta V$ . Consequently, the ESR signals are expected to be more intense than those of PMR.

The mechanism of transition from the lower level to the upper level is similar to that of PMR. The magnetic moment vector precesses around the magnetic field with a frequency equal to the angular frequency separation between the electronic spin energy levels. Thus, the transition of electron from one level to another can be achieved by generating a secondary magnetic field which revolves around the main magnetic field with a frequency equal to that of precessing electron.

The ESR signals like PMR signals can be achieved in two ways: (i) varying the field strength keeping the frequency of the oscillator constant, and (ii) varying the frequency of the oscillator keeping the external magnetic field constant. As in the case of PMR, it is preferred to use a fixed frequency supplied by an oscillator and to vary the external magnetic field. In actual practice, the ESR signals have finite width because of the larger relaxation time (time required for the electron to revert from the excited level to the ground level).<sup>†</sup> In order to improve accuracy,

<sup>†</sup> One of the reasons of observing wide signal is the Heisenberg uncertainty principle, according to which,  $\Delta E \cdot \Delta t \geq h/4\pi$ . Due to the finite lifetime of the excited state, its energy is not well defined and thus  $\Delta E$  does not have a single value but exhibits wide range. The linewidth of the signal is the width at half height of the absorption signal. The other factors causing line broadening are the Doppler effect (change in radiation frequency due to different component velocity of molecules in the direction of radiation), pressure broadening or collision broadening (change in stationary-state energy levels due to the varying intermolecular forces, also shortening of the lifetimes of excited states due to molecular collisions) and saturation broadening (change in population due to the intensity of radiation).

the signals are recorded as the derivative of the absorption curve with respect to the magnetic field. The type of derivative which one gets is shown in Fig. 4.3.4.

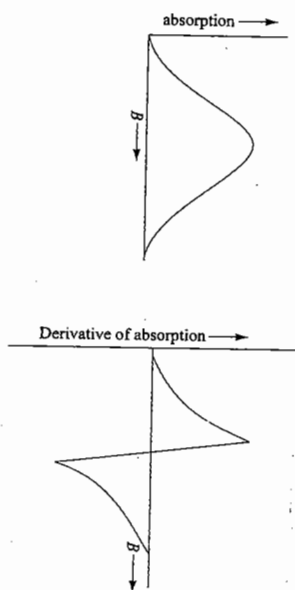


Fig. 4.3.4 ESR signal and its derivative

### Hyperfine Structures

The interaction of the magnetic moment of an electron with those of surrounding magnetic active nuclei results in the hyperfine structures in the ESR signals, i.e. a single absorption signal splits into more than one signal. The interaction energy depends on the relative direction of the magnetic moment of the electron relative to that of the proton. This interaction energy is expressed as  $am_I m_I$ , where  $a$  is a constant term, known as the *hyperfine coupling constant* or the *hyperfine splitting constant*. It represents the extent of interaction between the electron and the interacting nucleus.

The electronic energy including the above interaction energy becomes

$$V = g\mu_B m_s B + am_I m_I$$

Thus, for a given value  $m_s$ , the potential energy also depends on the value of  $m_I$ . For a proton, we have

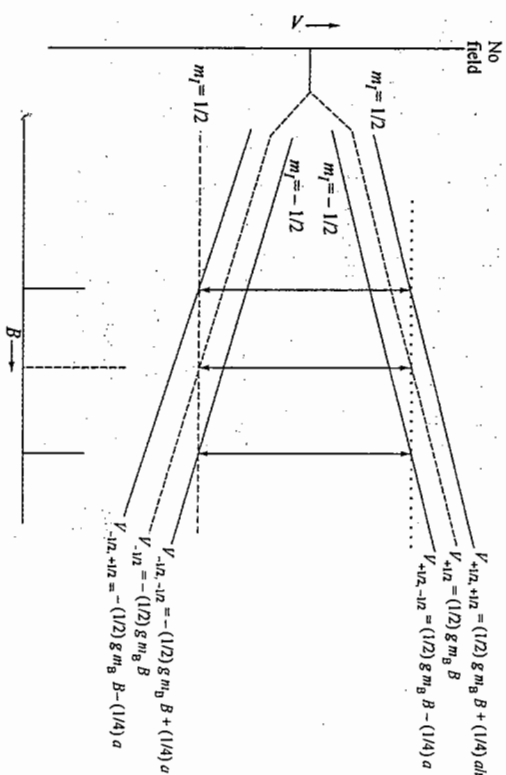
$$\begin{aligned} V_{+1/2, +1/2} &= (1/2)g\mu_B B + (1/4)a \\ V_{+1/2, -1/2} &= (1/2)g\mu_B B - (1/4)a \\ V_{-1/2, -1/2} &= -(1/2)g\mu_B B + (1/4)a \\ V_{-1/2, +1/2} &= -(1/2)g\mu_B B - (1/4)a \end{aligned}$$

where the first subscript represents the value of  $m_s$ , and the second that of  $m_I$ . The variations of these potential energies with the external magnetic field are shown in Fig. 4.3.5. The broken lines represent energies in the absence of interactions. The value of  $B$  at which absorptions are expected (only schematic) are shown at the foot of the figure.

The selection rules for the electron magnetic transitions are  $\Delta m_s = 1$  and  $\Delta m_I = 0$ , i.e. during the transition from  $m_s = -1/2$  to  $m_s = +1/2$ , the directions of the associated nuclear spins remain unchanged. Thus, if the system as shown in Fig. 4.3.5 is radiated with a constant magnetic field it will show two transitions of energies

$$\begin{aligned} E_1 &= g\mu_B B - (1/2)a; & m_I &= -1/2 \\ E_2 &= g\mu_B B + (1/2)a; & m_I &= +1/2 \end{aligned}$$

Fig. 4.3.5 Variation of potential energy of an electron in a varying magnetic field



The separation between these two absorptions is  $a$ . Thus, the constant  $a$  represents the separation between the two hyperfine lines of the ESR spectrum. In terms of frequency unit, we have

$$v_1 = \frac{g\mu_B B}{h} - \frac{1}{2} \frac{a}{h}; \quad m_I = -1/2$$

$$\text{and } v_2 = \frac{g\mu_B B}{h} + \frac{1}{2} \frac{a}{h}; \quad m_I = +1/2$$

In terms of magnetic field, we have

$$B_1 = \frac{hv}{g\mu_B} - \frac{a}{2g\mu_B}; \quad m_I = +1/2$$

$$\text{and } B_2 = \frac{hv}{g\mu_B} + \frac{a}{2g\mu_B}; \quad m_I = -1/2$$

For example, the ESR spectrum of the hydrogen atom produced by electric discharge or trapped in solids shows two ESR first-derivative signals with separation of about 0.05 T.

The energy of an unpaired electron coupled with two nuclei is given by

$$V = g\mu_B m_s B + a_1 m_s m_{I1} + a_2 m_s m_{I2}$$

where  $a_1$  and  $a_2$  are the coupling constants of the electron interacting with nuclei 1 and 2, and  $m_{I1}$  and  $m_{I2}$  are the quantum numbers of the component of the nuclear spins 1 and 2, respectively.

For the coupling with the two protons, each electronic level will split into a quartet. These are

$$\begin{aligned}
 V_{-1/2, +1/2, +1/2} &= -(1/2) g \mu_B B - (1/4) a_1 - (1/4) a_2 \\
 V_{-1/2, +1/2, -1/2} &= -(1/2) g \mu_B B - (1/4) a_1 + (1/4) a_2 \\
 V_{-1/2, -1/2, +1/2} &= -(1/2) g \mu_B B + (1/4) a_1 - (1/4) a_2 \\
 V_{-1/2, -1/2, -1/2} &= -(1/2) g \mu_B B + (1/4) a_1 + (1/4) a_2 \\
 V_{+1/2, -1/2, -1/2} &= (1/2) g \mu_B B - (1/4) a_1 - (1/4) a_2 \\
 V_{+1/2, -1/2, +1/2} &= (1/2) g \mu_B B - (1/4) a_1 + (1/4) a_2 \\
 V_{+1/2, +1/2, -1/2} &= (1/2) g \mu_B B + (1/4) a_1 - (1/4) a_2 \\
 V_{+1/2, +1/2, +1/2} &= (1/2) g \mu_B B + (1/4) a_1 + (1/4) a_2
 \end{aligned}$$

where the first subscript represents the value of  $m_s$  and the second and third those of  $m_{I1}$  and  $m_{I2}$ , respectively (Fig. 4.3.6).

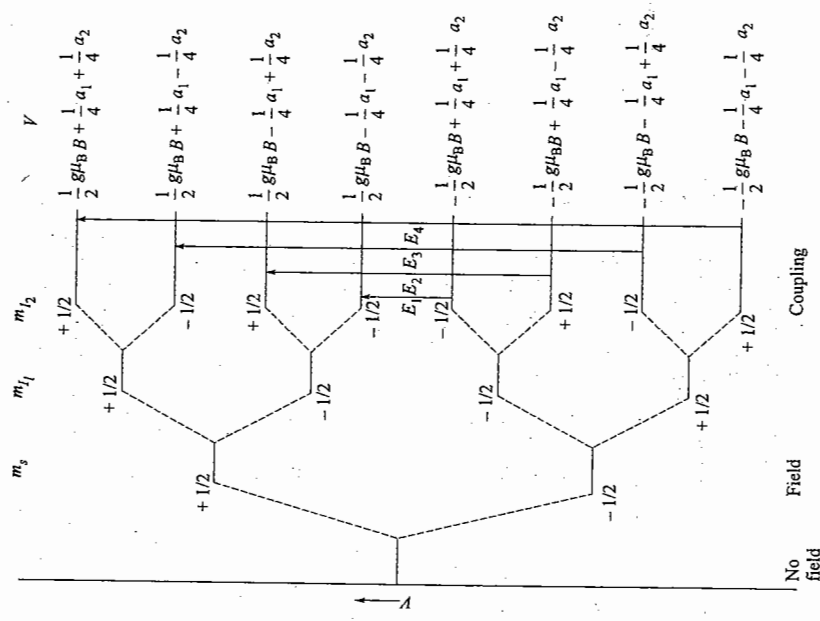


Fig. 4.3.6 Interaction of the electron with two protons with  $a_1 > a_2$

Following the selection rules ( $\Delta m_s = 1$  and  $\Delta m_l = 0$ ), the energies of four absorption lines observed will be

$$\begin{aligned}
 E_1 &= g \mu_B B - (1/2) a_1 - (1/2) a_2; \quad m_{I1} = -1/2, \quad m_{I2} = -1/2 \\
 E_2 &= g \mu_B B - (1/2) a_1 + (1/2) a_2; \quad m_{I1} = -1/2, \quad m_{I2} = +1/2 \\
 E_3 &= g \mu_B B + (1/2) a_1 - (1/2) a_2; \quad m_{I1} = +1/2, \quad m_{I2} = -1/2 \\
 E_4 &= g \mu_B B + (1/2) a_1 + (1/2) a_2; \quad m_{I1} = +1/2, \quad m_{I2} = +1/2
 \end{aligned}$$

If the frequency is held constant, the four signals will be observed at the following magnetic fields:

$$\begin{aligned}
 B_1 &= \frac{h\nu}{g\mu_B} - \frac{a_1}{2g\mu_B} - \frac{a_2}{2g\mu_B}; \quad m_{I1} = +1/2, \quad m_{I2} = +1/2 \\
 B_2 &= \frac{h\nu}{g\mu_B} - \frac{a_1}{2g\mu_B} + \frac{a_2}{2g\mu_B}; \quad m_{I1} = +1/2, \quad m_{I2} = -1/2 \\
 B_3 &= \frac{h\nu}{g\mu_B} + \frac{a_1}{2g\mu_B} - \frac{a_2}{2g\mu_B}; \quad m_{I1} = -1/2, \quad m_{I2} = +1/2 \\
 B_4 &= \frac{h\nu}{g\mu_B} + \frac{a_1}{2g\mu_B} + \frac{a_2}{2g\mu_B}; \quad m_{I1} = -1/2, \quad m_{I2} = -1/2
 \end{aligned}$$

Three cases may be distinguished on the basis of the relative magnitudes of  $a_1$  and  $a_2$ . These are:

- (i)  $a_1 > a_2$ : Four lines of equal intensities will be observed.
- (ii)  $a_1 \gg a_2$ : If  $a_2$  has a negligible value, then the interaction with the nucleus 2 may be neglected. The two lines which are observed due to the interaction with the nucleus 1 are

$$B_1 = \frac{h\nu}{g\mu_B} - \frac{a_1}{2g\mu_B}; \quad m_{I1} = 1/2$$

$$B_2 = \frac{h\nu}{g\mu_B} + \frac{a_1}{2g\mu_B}; \quad m_{I1} = -1/2$$

Each line will be twice as intense as the corresponding line in the case (i) discussed above.

- (iii)  $a_1 = a_2$ . Three lines will be observed at

$$B_1 = \frac{h\nu}{g\mu_B} - \frac{a}{g\mu_B}; \quad m_{I1} = +1/2, \quad m_{I2} = +1/2$$

$$B_2 = \frac{h\nu}{g\mu_B}; \quad \begin{cases} m_{I1} = +1/2, m_{I2} = -1/2 \\ m_{I1} = -1/2, m_{I2} = +1/2 \end{cases}$$

$$\text{and } B_3 = \frac{h\nu}{g\mu_B} + \frac{a}{g\mu_B}; \quad m_{I1} = -1/2, \quad m_{I2} = -1/2$$

The second line will be twice as intense as the other two, i.e. their relative ratio will be 1 : 2 : 1. The present case is also illustrated in Fig. 4.3.7.

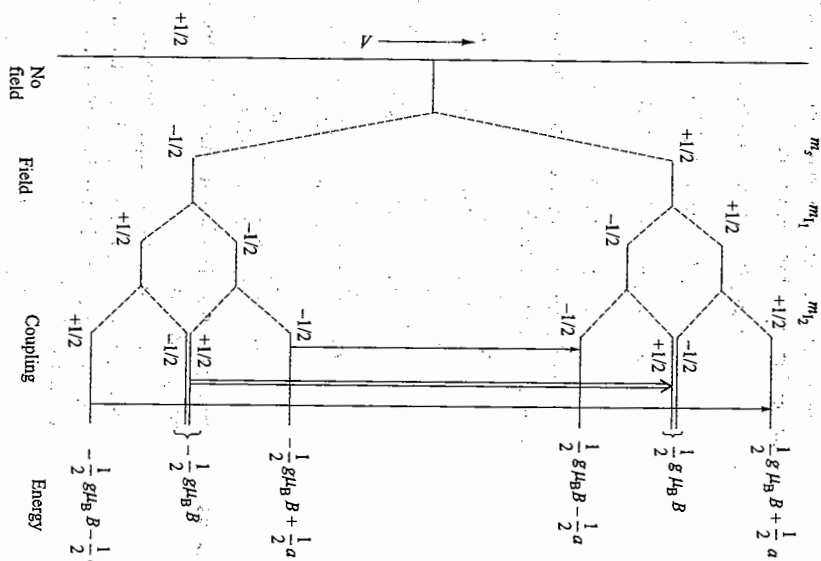


Fig. 4.3.7 Interaction of an electron with two identical protons

### Interaction with $n$ Nuclei

The energy expression will be given by

$$V = g \mu_B m_s B + a_1 m_s m_{I1} + a_2 m_s m_{I2} + \dots + a_n m_s m_{In}$$

and the resonance condition is given by

$$h\nu = g \mu_B B + a_1 m_{I1} + a_2 m_{I2} + \dots + a_n m_{In} \quad (4.3.9)$$

The number of  $m_I$  is given by the relation  $2I + 1$ , where  $I$  is the spin quantum number of the nucleus. Thus, the interaction of an electron with  $n$  nuclei gives rise to  $N$  transitions, where

$$N = (2I_1 + 1)(2I_2 + 1) \dots (2I_n + 1) \quad (4.3.10)$$

A special case of interest is worth mentioning here. This is when all the  $n$  protons are identical, i.e.  $a_1 = a_2 = \dots = a_n$ . The resonance condition is

$$h\nu = g \mu_B B + a(m_{I1} + m_{I2} + \dots + m_{In}) \quad (4.3.11)$$

If  $\nu$  is held constant, the values of  $B$  at which absorptions are expected are given by the expression

$$B = B_0 - a'(m_{I1} + m_{I2} + \dots + m_{In})$$

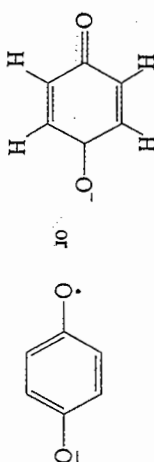
Since for a proton the permitted values of  $m_I$  are  $+1/2$  and  $-1/2$ , the sum in the above parenthesis can have  $(n+1)$  different values as given by

$$\frac{n}{2}, \frac{n}{2} - 1, \dots, -\left(\frac{n}{2} - 1\right), -\frac{n}{2}$$

Thus, the expected number of lines are  $(n+1)$ . All of them will be equidistant from each other. The intensity of an absorption line will be directly proportional to the degree of degeneracy of the involved levels. The relative intensities may be computed from

$${}^nC_m = \frac{n!}{m!(n-m)!}$$

where  $m = 0, 1, \dots, n$ . The above scheme may be illustrated with the example of  $p$ -benzoquinone radical anion.



It has four identical protons. Thus, we may expect five absorption lines with relative intensities as  ${}^4C_0 : {}^4C_1 : {}^4C_2 : {}^4C_3 : {}^4C_4$ , i.e.  $1 : 4 : 6 : 4 : 1$ . Its spectrum is shown in Fig. 4.3.8.

The benzene anion radical may be prepared by the chemical reduction of benzene with alkali metal in an inert solvent such as 1,2-dimethoxyethane or tetrahydrofuran. It contains 6 equivalent protons and thus its ESR spectrum includes seven lines with relative intensities  $1 : 6 : 15 : 20 : 15 : 6 : 1$  with a hyperfine splitting constant of  $3.75 \times 10^{-4}$  T.

The unpaired electron in benzene anion radical is present in the antibonding  $\pi$ -molecular orbital which has a node in the plane of the molecule. Due to this, the carbon atoms have zero-electron densities. However, this  $\pi$ -electron can polarize electron pairs of C—H bond, causing hydrogen atom to have a some unpaired spin density which accounts for the small value of hyperfine splitting constant. A useful relation between hyperfine splitting constant ( $a$ ) and the unpaired spin density ( $\rho$ ) on the carbon atom to which the proton is attached is due to McConnell:

$$a_H = Q\rho_{\pi C}$$

where  $Q$  is called the spin-polarization parameter. For  $\pi$  radicals, its value is  $0.0025$  T.

For methyl radical, the value of  $\rho_{\pi C}$  will be equal to one. Hence, the hyperfine splitting constant of methyl protons is expected to be  $0.0025$  T.

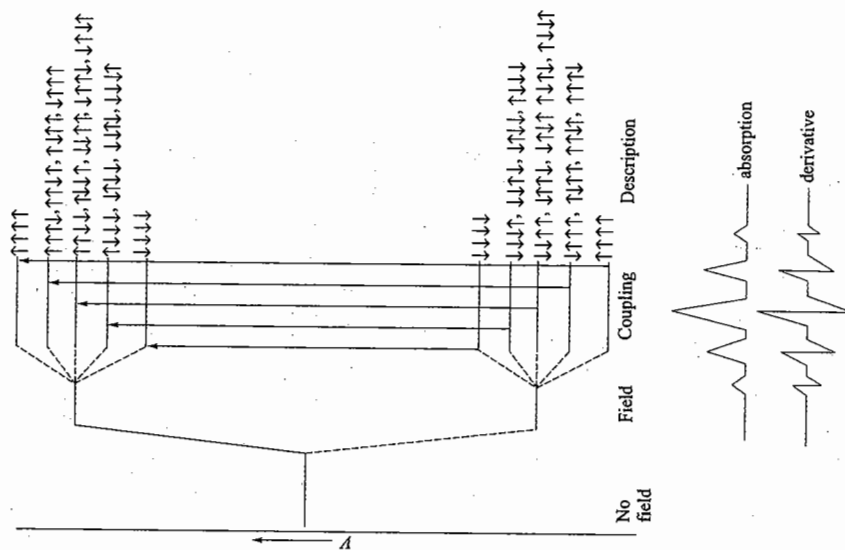


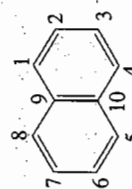
Fig. 4.3.8 ESR spectrum of *p*-benzoquinone radical anion

### Example 4.3.1

How many ESR absorption lines do you expect for naphthalene negative ion? If the lowest unoccupied molecular orbital of naphthalene is of the form

$$\psi_6 = 0.4253 [\psi_{2p_z(1)} + \psi_{2p_z(4)} - \psi_{2p_z(5)} - \psi_{2p_z(8)}] + 0.2629 [-\psi_{2p_z(2)} - \psi_{2p_z(3)} + \psi_{2p_z(6)} + \psi_{2p_z(7)}]$$

where numbering of carbon atoms in naphthalene goes as follows.



Predict the values of hyperfine splitting constants due to  $\alpha$  and  $\beta$  carbon atoms.

### Solution

Naphthalene has two kinds of protons, each containing four protons. Hence, we expect five absorptions due to interaction with one kind of protons and each of these five absorptions will further split into five due to the interaction with second kind of protons. Thus, there will be a total of 25 absorptions ( $= 5 \times 5$ ).

The hyperfine splitting constants of these two kinds of protons can be estimated by using McConnell relation,  $a_H = Q \rho_{\pi,C}$

The  $\pi$ -electron spin density on each of carbons 1, 4, 5 and 8 will be  $0.4253^2$  which is 0.1809. Hence,

$$a = Q \rho_{\pi,C} = (25 \times 10^{-4} \text{ T}) (0.1809) = 4.52 \times 10^{-4} \text{ T}$$

The  $\pi$ -electron spin density on each of carbons 2, 3, 6 and 7 will be  $0.2629^2$  which is 0.06912.

$$\text{Hence } a = Q \rho_{\pi,C} = (25 \times 10^{-4} \text{ T}) (0.06912) = 1.73 \times 10^{-4} \text{ T.}$$

The observed values are  $4.94 \times 10^{-4} \text{ T}$  and  $1.83 \times 10^{-4} \text{ T}$ , respectively.

### Example 4.3.2

### Solution

The benzene radical anion  $C_6H_6^-$  has a  $g$ -value of 2.0025. At what field would you search for resonance in a spectrometer operating at 9.302 GHz?

We have

$$\nu = 9.302 \text{ GHz} = 9.302 \times 10^9 \text{ s}^{-1}$$

$$\Delta V = h\nu = (6.626 \times 10^{-34} \text{ J s}) (9.302 \times 10^9 \text{ s}^{-1}) = 6.164 \times 10^{-24} \text{ J}$$

Now since,  $\Delta V = g \mu_B B$ , we have

$$B = \frac{\Delta V}{g \mu_B} = \frac{(6.164 \times 10^{-24} \text{ J})}{(2.0025)(9.2741 \times 10^{-24} \text{ J T}^{-1})} = 0.332 \text{ T}$$

A radical containing two nonequivalent protons with splitting constants 2.0 mT and 2.6 mT gives a spectrum centred on 332.5 mT. At what fields do the hyperfine lines lie, and what are their relative intensities?

The fields of hyperfine lines can be computed from the expression

$$B = B_0 + a_1 m_{I_1} + a_2 m_{I_2} \quad (\text{Eq. 4.3.9})$$

where we can identify  $a_1 = 2.0 \text{ mT}$ , and  $a_2 = 2.6 \text{ mT}$ . Each quantum number  $m_{I_1}$  and  $m_{I_2}$ , can have values of  $+1/2$  and  $-1/2$ . Thus, we expect to observe lines at the following fields.

$$B_1 = 332.5 \text{ mT} + (2.0 \text{ mT}) (1/2) + (2.6 \text{ mT}) (1/2) = 334.8 \text{ mT}$$

$$B_2 = 332.5 \text{ mT} + (2.0 \text{ mT}) (1/2) + (2.6 \text{ mT}) (-1/2) = 332.2 \text{ mT}$$

$$B_3 = 332.5 \text{ mT} + (2.0 \text{ mT}) (-1/2) + (2.6 \text{ mT}) (1/2) = 332.8 \text{ mT}$$

$$B_4 = 332.5 \text{ mT} + (2.0 \text{ mT}) (-1/2) + (2.6 \text{ mT}) (-1/2) = 330.2 \text{ mT}$$

All the four lines will be equally intense.

### Example 4.3.4

### Solution

Predict the form of ESR spectrum of a radical containing one  $^{14}\text{N}$  nucleus ( $I = 1$ ,  $a = 1.03 \text{ mT}$ ) and two equivalent protons ( $I = 1/2$ ,  $a = 0.35 \text{ mT}$ ).

Due to  $^{14}\text{N}$ , the ESR line will split into three lines ( $2I + 1 = 3$ ) of equal intensities with the separation of 1.03 mT. Each line will further split into three lines due to the presence of two equivalent protons. The separation between them will be 0.35 mT and have

relative intensities of 1 : 2 : 1. Thus, the overall pattern will have three equivalent 1 : 2 : 1 triplets each with internal splitting 0.35 mT and separated from its neighbour by 1.03 mT.

### Example 4.3.5

Predict the intensity distribution in the hyperfine lines of the ESR spectrum of the radical  $\text{CD}_3$  ( $I = 1$  for D).

Each of the two energy levels of electron will show the splitting as shown in Fig. 4.3.9. Thus, the ESR signal will include seven lines with relative intensities of 1 : 3 : 6 : 7 : 6 : 3 : 1.

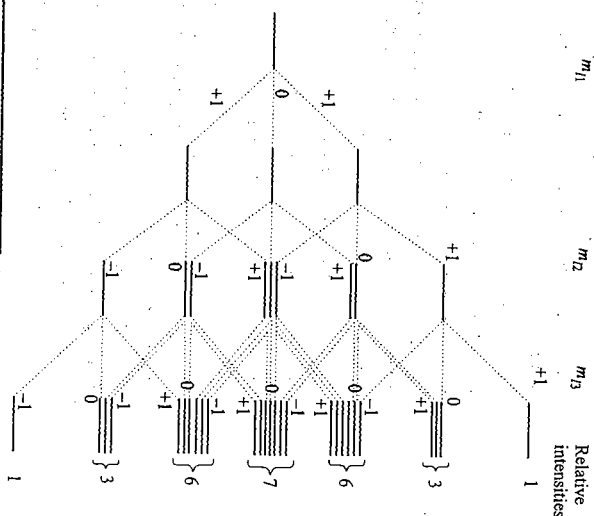


Fig. 4.3.9

### Example 4.3.6

#### Solution

Predict the appearance of the ESR spectrum of the ethyl radical. Given:  $a(\text{CH}_2) = 0.224$  mT and  $a(\text{CH}_3) = 0.268$  mT.

The ethyl radical contains two types of protons, viz., methylene and methyl protons. Due to the methylene protons, the ESR line will split into three lines of relative intensities 1 : 2 : 1. Each of these three lines will split into four lines due to the methyl protons with relative intensities 1 : 3 : 3 : 1. Thus, the ethyl radical will show twelve lines, i.e., quartet (1 : 3 : 3 : 1) of triplets (1 : 2 : 1).

For identical protons, the ESR lines are observed at

$$\frac{h\nu}{g\mu_B} = B_0 + a(m_1 + m_2 + \dots) \quad (4.3.11)$$

For methylene protons  $\Sigma m_i$  have the values of +1, 0 and -1. Hence, the lines with relative intensities 1 : 2 : 1 will be observed at

$$B_1 = B_0 + 0.224 \text{ mT}$$

$$B_2 = B_0$$

$$B_3 = B_0 - 0.224 \text{ mT}$$

For methyl protons  $\Sigma m_i$  have the values of  $3/2$ ,  $1/2$ ,  $-1/2$  and  $-3/2$ . Thus, each of the above three lines will split into four lines at the following magnetic fields.

$$B_{11} = B_0 + (0.224 \text{ mT}) + (0.268 \text{ mT}) (3/2) = B_0 + (0.626 \text{ mT})$$

$$B_{12} = B_0 + (0.224 \text{ mT}) + (0.268 \text{ mT}) (1/2) = B_0 + (0.358 \text{ mT})$$

$$B_{13} = B_0 + (0.224 \text{ mT}) + (0.268 \text{ mT}) (-1/2) = B_0 + (0.09 \text{ mT})$$

$$B_{14} = B_0 + (0.224 \text{ mT}) + (0.268 \text{ mT}) (-3/2) = B_0 - (0.178 \text{ mT})$$

The relative intensities of these lines will be 1 : 3 : 3 : 1, respectively,

$$B_{21} = B_0 + (0.268 \text{ mT}) (3/2) = B_0 + (0.402 \text{ mT})$$

$$B_{22} = B_0 + (0.268 \text{ mT}) (1/2) = B_0 + (0.134 \text{ mT})$$

$$B_{23} = B_0 + (0.268 \text{ mT}) (-1/2) = B_0 - (0.13 \text{ mT})$$

$$B_{24} = B_0 + (0.268 \text{ mT}) (-3/2) = B_0 - (0.402 \text{ mT})$$

The relative intensities of these lines will be 2 : 6 : 6 : 2, respectively.

$$B_{31} = B_0 - (0.224 \text{ mT}) + (0.268 \text{ mT}) (3/2) = B_0 + (0.178 \text{ mT})$$

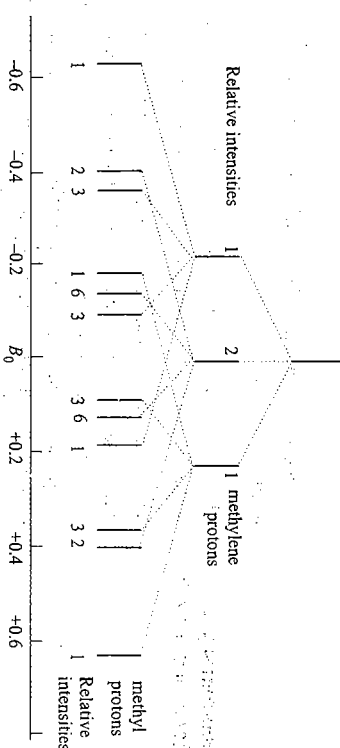
$$B_{32} = B_0 - (0.224 \text{ mT}) + (0.268 \text{ mT}) (1/2) = B_0 - (0.09 \text{ mT})$$

$$B_{33} = B_0 - (0.224 \text{ mT}) + (0.268 \text{ mT}) (-1/2) = B_0 - (0.358 \text{ mT})$$

$$B_{34} = B_0 - (0.224 \text{ mT}) + (0.268 \text{ mT}) (-3/2) = B_0 - (0.626 \text{ mT})$$

The relative intensities of these lines will be 1 : 3 : 3 : 1, respectively. If these lines are arranged in the increasing order of  $B$ , the relative intensities will be 1 : 2 : 3 : 1 : 6 : 3 : 3 : 6 : 1 : 3 : 2 : 1, respectively, as shown in Fig. 4.3.10.

Fig. 4.3.10



## 4.4 ROTATIONAL SPECTRA OF DIATOMIC MOLECULES

### Introduction

The absorption spectrum in the microwave region corresponds to the promotion of a molecule from its lower rotational level to the higher ones. The correlation of experimental absorption with the theoretical difference in energy levels yields information regarding the interatomic distances of gaseous diatomic molecules.



### Expression of Rotational Energies

While dealing with the rotational energies of diatomic molecules in Section 1.6, we have replaced a diatomic molecule by a rigid rotator model. In this model, a gaseous molecule is represented by a dumb-bell having two balls of masses  $m_1$  and  $m_2$  (representing the masses of the atoms) which are connected to each other by a rigid rod of length  $r$  (representing the distance between the two atoms in the molecule). It was seen that the rotational energies of diatomic molecules are quantized and are given by the expression

$$E = \frac{h^2}{8\pi^2 I} J(J+1) \quad (4.4.1)$$

where  $I$  is the moment of inertia of the molecule and  $J$  is the rotational quantum number which can have integral values of 0, 1, 2, 3, .... The moment of inertia is given by

$$I = \mu r^2 \quad (4.4.2)$$

here  $\mu$ , the reduced mass, is given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}, \quad \text{i.e.} \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad (4.4.3)$$

It may be noticed that the energy expression (Eq. 4.4.1) may be obtained by introducing the quantization condition of angular momentum in the classical expression of kinetic energy, i.e.

$$E_k = \frac{1}{2} I \omega^2 = \frac{1}{2} \frac{(I\omega)^2}{I} = \frac{1}{2} \frac{L^2}{I} \quad (4.4.4)$$

where  $L$  is the angular momentum whose quantized values are given by

$$L = \sqrt{J(J+1)} \left( \frac{h}{2\pi} \right); \quad J = 0, 1, 2, 3, \dots \quad (4.4.5)$$

Thus on substituting Eq. (4.4.5) in Eq. (4.4.4), we get the energy expression as given by Eq. (4.4.1).

### Degeneracy of Rotational Levels

The condition of quantization of angular momentum means that a diatomic molecule cannot rotate with any arbitrary angular velocity but with a velocity that leads to any of the quantized values of angular momentum of  $0, \sqrt{2}(h/2\pi), \sqrt{6}(h/2\pi), \dots$ , and so on. The angular momentum, being a vector quantity, also has a direction which acts along the axis of rotation. The latter lies perpendicular to the plane of rotation of the molecule. In Section 1.6, it was also seen that there occurs space quantization of angular momentum vector, i.e. the angular momentum vector cannot have any arbitrary direction in space but can have only a few selective orientations as dictated by the quantization condition of the component of angular momentum vector along a given reference direction. The latter is conveniently defined by the direction of an external magnetic field and is labelled as the  $z$ -axis. These orientations are characterized by the magnetic quantum number  $m_J$  which determines the allowed values of  $z$ -component of angular momentum, i.e.  $m_J(h/2\pi)$ . For a given value of  $J$ , the allowed values of  $m_J$  are

$$J, (J-1), \dots, 0, \dots, -(J-1), -J$$

Thus, a molecule can have  $(2J+1)$  orientations of its angular momentum vector or in other words, it can have  $(2J+1)$  orientations in space and thus  $(2J+1)$  different axes of rotation. The energy of the rotator depends only on the quantum number  $J$  and thus all these  $(2J+1)$  orientations are degenerate. Figure 4.4.1 depicts the orientations of angular momentum vectors for  $J=1$  and  $J=2$ . For  $J=1$ , we have three different directions of angular momentum and thus three different axes of rotation. The rotations around these three axes carry the same amount of rotational energy. Similarly for  $J=2$ , we have five different directions of angular momentum vector and thus the energy levels are 5-fold degenerate.

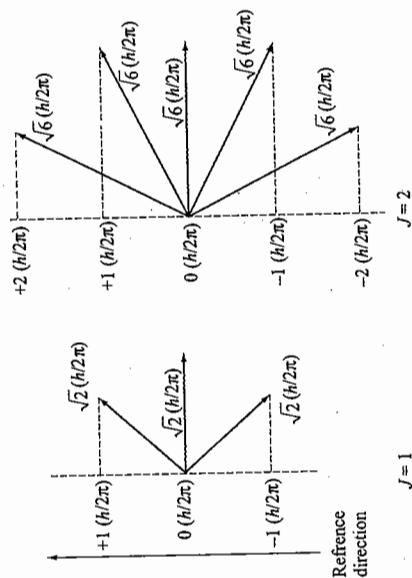


Fig. 4.4.1 Orientations of angular momentum vectors for  $J=1$  and  $J=2$

### Energy Level Diagram

The allowed rotational energies are given by the expression

$$E = \frac{h^2}{8\pi^2 I} J(J+1); \quad J = 0, 1, 2, 3, \dots \quad (\text{Eq. 4.4.1})$$

In the frequency unit, we have

$$\nu = \frac{h}{8\pi^2 I} J(J+1); \quad J = 0, 1, 2, 3, \dots \quad (4.4.6)$$

and in the wavenumber unit, we have

$$\begin{aligned} \tilde{E} &= \frac{h}{8\pi^2 I c} J(J+1) \\ &= B J(J+1); \quad J = 0, 1, 2, 3, \dots \end{aligned} \quad (4.4.7)^\dagger$$

where  $B = h/8\pi^2 I c$  and is known as the *rotational constant*. The approximate order of the value of  $B$  may be seen from the following calculations on CO and HBr.

<sup>†</sup> The rotational energy expressed in wavenumber unit is known as rotational term (symbol:  $F$ ), i.e.  $F = E/hc$ .

**Carbon monoxide** For CO,  $r_{\text{CO}} = 113$  pm. The reduced mass is

$$\mu_{\text{CO}} = \frac{m_{\text{C}}m_{\text{O}}}{m_{\text{C}} + m_{\text{O}}} = \frac{\{(0.012 \text{ kg})/(6.023 \times 10^{23})\}\{(0.016 \text{ kg})/(6.023 \times 10^{23})\}}{\{(0.012 \text{ kg})/(6.023 \times 10^{23})\} + \{(0.016 \text{ kg})/(6.023 \times 10^{23})\}}$$

$$= 1.14 \times 10^{-26} \text{ kg}$$

Thus, its moment of inertia is

$$I = \mu r^2 = (1.14 \times 10^{-26} \text{ kg}) (113 \times 10^{-12} \text{ m})^2$$

$$= 14.5 \times 10^{-47} \text{ kg m}^2$$

Hence  $B = \frac{h}{8\pi^2 I c} = \frac{(6.626 \times 10^{-34} \text{ J s})}{8(3.14)^2 (14.5 \times 10^{-47} \text{ kg m}^2) (2.998 \times 10^8 \text{ m s}^{-1})}$

$$= 1.932 \times 10^2 \text{ m}^{-1}$$

The value of rotational constant in joule is

$$Bhc = (1.932 \times 10^2 \text{ m}^{-1}) (6.626 \times 10^{-34} \text{ J s}) (2.998 \times 10^8 \text{ m s}^{-1})$$

$$= 3.838 \times 10^{-23} \text{ J}$$

**Hydrogen bromide** For HBr,  $r_{\text{HBr}} = 141$  pm. Thus, we have

$$\mu_{\text{HBr}} = \frac{m_{\text{H}}m_{\text{Br}}}{m_{\text{H}} + m_{\text{Br}}} = \frac{\{(0.001 \text{ kg})/(6.023 \times 10^{23})\}\{(0.0799 \text{ kg})/(6.023 \times 10^{23})\}}{\{(0.001 \text{ kg})/(6.023 \times 10^{23})\} + \{(0.0799 \text{ kg})/(6.023 \times 10^{23})\}}$$

$$= 1.64 \times 10^{-27} \text{ kg}$$

$$I_{\text{HBr}} = \mu r^2 = (1.64 \times 10^{-27} \text{ kg}) (141 \times 10^{-12} \text{ m})^2$$

$$= 3.26 \times 10^{-47} \text{ kg m}^2$$

$$B = \frac{h}{8\pi^2 I c} = \frac{(6.626 \times 10^{-34} \text{ J s})}{8(3.14)^2 (3.26 \times 10^{-47} \text{ kg m}^2) (2.998 \times 10^8 \text{ m s}^{-1})}$$

$$= 8.595 \times 10^2 \text{ m}^{-1}$$

The value of rotational constant in joule is

$$Bhc = (8.595 \times 10^2 \text{ m}^{-1}) (6.626 \times 10^{-34} \text{ J s}) (2.998 \times 10^8 \text{ m s}^{-1})$$

$$= 1.707 \times 10^{-22} \text{ J}$$

The various allowed rotational energy levels for these two molecules are shown in Fig. 4.4.2.

The relative populations of energy levels can be computed by the Boltzmann equation

$$\frac{n_2}{n_1} = \exp(-\Delta E/kT) \quad (4.4.8)$$

where  $n_1$  and  $n_2$  are the number of molecules in the lower and upper levels, respectively, and  $\Delta E$  is the energy difference between the two levels. The population in each level is given by the expression

$$n_j \propto \exp(-E_j/kT) \quad (4.4.9)$$

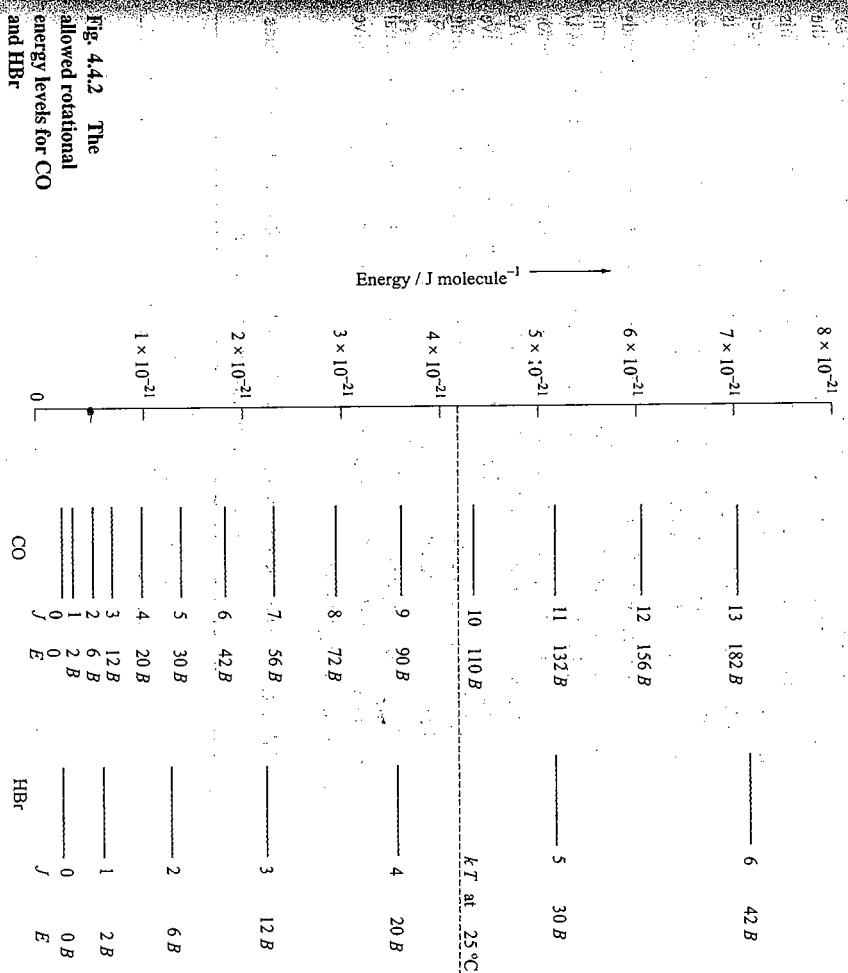


Fig. 4.4.2 The allowed rotational energy levels for CO and HBr

Since the molecule can rotate in  $2J + 1$  different planes with the same rotational energy, the various rotational energy states are degenerate by a factor of  $2J + 1$ . This factor is known as the multiplicity of energy level and is written as  $g_J$ . The probability of occupancy of these degenerate states are completely identical and thus all the degenerate states are equally populated. Incorporating this multiplicity factor in Eq. (4.4.9), we get

$$n_J \propto g_J \exp(-E_J/kT) \quad (4.4.10)$$

From Eq. (4.4.10), we may write

$$\frac{n_{J'}}{n_{J''}} = \frac{(2J' + 1) \exp(-E_{J'}/kT)}{(2J'' + 1) \exp(-E_{J''}/kT)} = \frac{(2J' + 1)}{(2J'' + 1)} \exp(-\Delta E/kT) \quad (4.4.11)$$

where  $J'$  and  $J''$  are the rotational quantum numbers of the higher and lower energy levels, respectively.

A qualitative discussion regarding the relative populations of various energy levels may be made here. At the very outset, it may be concluded that many of the lower rotational levels are expected to be thickly populated since  $\Delta E_J = kT$ . This follows immediately from the fact that the thermal energy, which is much larger than the energy difference of many lower levels with respect to  $J = 0$  level, is sufficient to promote the molecules from the energetically most stable level (i.e.  $J = 0$  for which  $E_J = 0$ ) to the higher ones (Fig. 4.4.2).

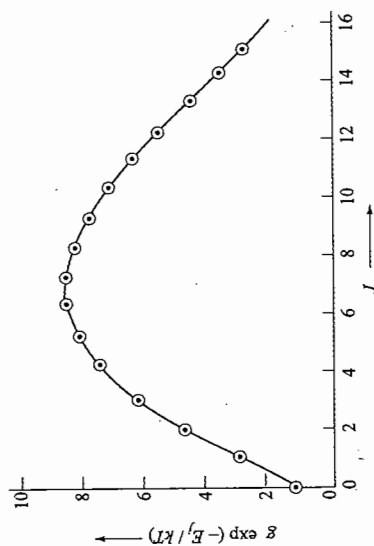
Now according to Eq. (4.4.10), the number of molecules in any level depends on two factors, viz., the multiplicity factor  $2J + 1$  and the exponential term  $\exp(-E_J/kT)$ . These two factors have altogether different characteristics. As  $J$  increases, the multiplicity factor increases steadily whereas the exponential factor decreases slowly in the beginning and more rapidly with the higher values of  $J$ . As a consequence of these two factors, the number of molecules (or the relative population with respect to  $J = 0$  level) in the various levels increases in the beginning and after passing through the maximum, it decreases.

Table 4.4.1 depicts the results of calculation on CO, for which the rotational constant  $B = 3.838 \times 10^{-23}$  J. Figure 4.4.3 shows the corresponding plots of relative populations against the value of  $J$ .

**Table 4.4.1** The Value of  $g_J \exp(-E_J/kT)$  for CO at 298 K for different Values of Rotational Quantum Number

$J$	$g_J = (2J + 1)$	$E_J = \frac{Bhc}{10^{-23}} J(J + 1)$	$\exp(-E_J/kT)$	$g_J \exp(-E_J/kT)$
0	1	0		
1	3	$2B = 7.68$	0.982	2.945
2	5	$6B = 23.03$	0.945	4.727
3	7	$12B = 46.07$	0.894	6.259
4	9	$20B = 76.78$	0.830	7.466
5	11	$30B = 115.17$	0.756	8.314
6	13	$42B = 161.24$	0.676	8.784
7	15	$56B = 214.98$	0.593	8.95
8	17	$72B = 276.41$	0.511	8.682
9	19	$90B = 345.51$	0.431	8.199
10	21	$110B = 422.29$	0.358	7.524
11	23	$132B = 506.75$	0.292	6.711
12	25	$156B = 598.88$	0.233	5.83
13	27	$182B = 698.70$	0.183	4.941
14	29	$210B = 806.19$	0.141	4.086
15	31	$240B = 921.36$	0.106	3.298

**Fig. 4.4.3** The relative populations in various rotational levels of CO at 298 K



The value of  $J$  (nearest integral) having maximum number of molecules can be determined by differentiating Eq. (4.4.10) with respect to  $J$  and then setting the resultant expression to zero.

Thus, we have

$$\frac{dn_J}{dJ} = \frac{d\{g_J \exp(-E_J/kT)\}}{dJ} = 0$$

This gives

$$\frac{d}{dJ} \{(2J + 1) \exp(-BhcJ(J + 1)/kT)\} = 0$$

$$\text{or } 2 \exp(-BhcJ(J + 1)/kT)$$

$$- (2J + 1) \frac{Bhc}{kT} (2J + 1) \exp(-BhcJ(J + 1)/kT) = 0$$

$$\text{or } 2 - (2J + 1)^2 \frac{Bhc}{kT} = 0$$

$$\text{or } J = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} \quad (4.4.12)$$

For CO at 298 K, the value of  $J$  is equal to

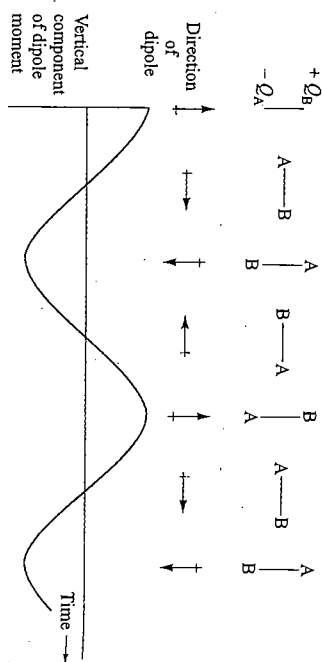
$$\left\{ \frac{1}{2} \frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{(3.38 \times 10^{-23} \text{ J})} \right\}^{1/2} - \frac{1}{2} = 7.32 - 0.5 = 6.82 \approx 7$$

This value is also in agreement with the data recorded in Table 4.4.1.

The interaction between the radiation and the rotating molecule is through the fluctuating electrical field of the radiation and the similar field generated by the rotation of the molecule. The electrical component of the radiation oscillates in a plane perpendicular to the direction of propagation of the wave. The frequency of this oscillating electrical component is equal to the frequency of the radiation. On the other hand, an oscillating electrical field is generated by the rotation of a molecule which has a *permanent dipole moment*. On rotation, the positive and negative ends of the molecule change places periodically and thus the component of dipole moment in a given direction such as the vertical component in the plane of the paper fluctuates periodically as shown in Fig. 4.4.4. The frequency of fluctuation of the component of dipole moment is equal to the frequency of rotation of the molecule.

#### Mechanism of Interaction between the Radiation and the Rotating Molecule

Fig. 4.4.4 Fluctuation in the vertical component of the dipole moment during the rotation of the molecule having a permanent dipole moment



When the frequency of fluctuation of the component of dipole moment (i.e. frequency of rotation of the molecule) becomes equal to that of the electric component of the radiation (i.e. the frequency of radiation itself), there occurs the phenomenon of resonance and hence energy can be transferred from the radiation to the molecule and vice versa. If the energy is absorbed by the molecule, it is promoted from a lower rotational level to a higher level. On the other hand, if the energy is given out, the molecule comes back from a higher level to a lower level.

A molecule having no permanent dipole moment does not generate the oscillating electrical field on rotation and hence cannot interact with the radiation. Such a molecule does not exhibit the rotational spectrum. Thus, *the essential criterion for a molecule to exhibit rotational spectrum is that it must have a permanent dipole moment*. The molecules with permanent dipole moment are known as *microwave active* molecules and those with no permanent dipole moment are known as *microwave inactive* molecules.

The homonuclear molecules such as  $H_2$ ,  $N_2$ ,  $O_2$ ,  $Cl_2$ , etc., have no permanent dipole moment and hence do not exhibit the rotational spectra. Molecules having centre of symmetry do not possess permanent dipole moment and hence also fall in the category of microwave inactive molecules. Examples include  $O=C=O$ ,  $S=C=S$ ,  $H-C\equiv C-H$ , etc. Molecules such as  $CH_4$  also do not have permanent dipole moment and thus are microwave inactive molecules.

The quantum mechanical calculations show that for a rigid rotator, the transition from one rotational level to another occurs with the condition of

$$\Delta J = \pm 1 \quad (4.4.13)$$

that is, the change in the rotational quantum number is unity.<sup>†</sup> Equation (4.4.13) In deriving the selection rule for rotational changes, the transition moment integral involves the term

$$\int_0^{2\pi} \int_0^\pi [Y_m^n]^* Y_{m'}^{n'} \cos \theta \sin \theta \, d\theta \, d\phi$$

$$\text{where } Y_m^n = \Theta_{J,m} \Phi_m = \left\{ \frac{(2J+1)(J-m)!}{2(J+m)!} \right\}^{1/2} P_m^J \left[ \frac{1}{\sqrt{2\pi}} e^{im\phi} \right]$$

Integration over  $\phi$  requires that  $m = m'$  for a nonzero value of the integral. Hence, the selection rule is  $\Delta m = 0$ . Integration over  $\theta$  requires that for  $m = m'$ , we must have  $\Delta J = \pm 1$  for a nonzero value of the integral.

#### Appearance of Rotational Spectrum

is, in fact, the selection rule for the rotational transitions. The probability of transition from any quantum level to the next higher level is the same and all other transitions are forbidden. For example, if a molecule is in the  $J = 0$  level, it can be promoted only to  $J = 1$  level and if it exists in  $J = 1$  level, it can be promoted with equal probability to  $J = 2$  level and so on.

The energy difference between the two rotational levels is

$$\Delta \tilde{E} = B J'(J' + 1) - B J''(J'' + 1) \quad (4.4.14)$$

where  $J'$  and  $J''$  are the rotational quantum numbers of higher and lower levels respectively. According to the selection rule, we have

$$J' = J'' + 1 \quad (4.4.15)$$

Substituting the above relation in Eq. (4.4.14), we get

$$\begin{aligned} \Delta \tilde{E} &= B(J'' + 1)(J'' + 2) - B J''(J'' + 1) \\ &= B(J'' + 1)(J'' + 2 - J'') \\ &= 2B(J'' + 1) \end{aligned} \quad (4.4.16)$$

Since many of the lower rotational levels are populated, it is expected that the pure rotational spectrum would consist of more than one absorption line. In fact, a series of absorption lines at the wave numbers listed in Table 4.4.2 are observed.

Table 4.4.2 Energies of Absorption Lines in a Rotational Spectrum

Transition	$\Delta \tilde{E} = 2B(J'' + 1)$
$J' = 1 \leftarrow J'' = 0$	$2B$
$J' = 2 \leftarrow J'' = 1$	$4B$
$J' = 3 \leftarrow J'' = 2$	$6B$
$J' = 4 \leftarrow J'' = 3$	$8B$
$J' = 5 \leftarrow J'' = 4$	$10B$
—	—
—	—
—	—

The spacing between any two nearest absorption signals is constant and is equal to  $2B$ . The intensities of all these transitions are not equal. It may be expected that the number of molecules promoted from a given level depends on its population, i.e. larger the population, larger the number of molecules that can be promoted to the next higher level, and hence larger the intensity of absorption. Thus, the expected relative intensities of various transitions follow the curve as shown at the foot of Fig. 4.4.5. There occurs a progressive increase in intensity in the beginning and after passing through a maximum, it diminishes.

The values of  $\mu$  for CO molecule is

$$\begin{aligned}\mu &= \frac{m_1 m_2}{m_1 + m_2} = \frac{\{(0.012 \text{ kg})/(6.023 \times 10^{23})\} \{(0.016 \text{ kg})/(6.023 \times 10^{23})\}}{\{(0.012 \text{ kg})/(6.023 \times 10^{23})\} + \{(0.016 \text{ kg})/(6.023 \times 10^{23})\}} \\ &= \frac{0.012 \times 0.016}{0.028 \times 6.023 \times 10^{23}} \text{ kg} = 1.14 \times 10^{-26} \text{ kg}\end{aligned}$$

$$\text{Hence } r = \left( \frac{I}{\mu} \right)^{1/2} = \left( \frac{1.458 \times 10^{-46} \text{ kg m}^2}{1.14 \times 10^{-26} \text{ kg}} \right)^{1/2}$$

$$= 1.13 \times 10^{-10} \text{ m} = 1.13 \times 10^{-8} \text{ cm} = 113 \text{ pm}$$

When a particular atom in a molecule is replaced by its isotope, the resultant molecule is found to be chemically identical to the original molecule. The internuclear distance and the electron distribution of the molecule do not change by the isotopic substitution and thus its dipole moment remains unaltered. However, there occurs an increase in the moment of inertia of the molecule. Since  $I$  appears in the denominator of the expression of  $B (= h/8\pi^2 Ic)$ , it follows that an increase in the value of  $I$  leads to a decrease in the value of  $B$ . This, in turn, decreases the energies of various rotational levels with the result that the energy levels become closer to one another. As a consequence of this, the spacing between the two absorption signals, which is equal to  $2B$ , is also decreased.

A closer examination of the rotational spectrum of gaseous molecules obtained by isotopic substitution helps not only to determine the atomic masses of isotopes but also their relative abundance from the comparison of absorption intensities.

The first rotational absorption of  $^{12}\text{C}^{16}\text{O}$  is found to occur at  $3.8424 \text{ cm}^{-1}$  while that of  $^{13}\text{C}^{16}\text{O}$  at  $3.6734 \text{ cm}^{-1}$ . Assuming the molar masses of  $^{16}\text{O}$  and  $^{12}\text{C}$  as  $15.9994 \text{ g mol}^{-1}$  and  $12.0000 \text{ g mol}^{-1}$  respectively, calculate the molar mass of  $^{13}\text{C}$ .

We are given that

$$2B_{^{12}\text{C}^{16}\text{O}} = 3.8424 \text{ cm}^{-1} \quad \text{and} \quad 2B_{^{13}\text{C}^{16}\text{O}} = 3.6734 \text{ cm}^{-1}$$

$$\text{Thus } B_{^{12}\text{C}^{16}\text{O}} = 1.9212 \text{ cm}^{-1} \quad \text{and} \quad B_{^{13}\text{C}^{16}\text{O}} = 1.8367 \text{ cm}^{-1}$$

Taking the ratio of the two  $B$ s, we have

$$\frac{B_{^{12}\text{C}^{16}\text{O}}}{B_{^{13}\text{C}^{16}\text{O}}} = \frac{h/8\pi^2 I_{^{12}\text{C}^{16}\text{O}} c}{h/8\pi^2 I_{^{13}\text{C}^{16}\text{O}} c} = \frac{I_{^{13}\text{C}^{16}\text{O}}}{I_{^{12}\text{C}^{16}\text{O}}} = \frac{\mu_{^{13}\text{C}^{16}\text{O}}}{\mu_{^{12}\text{C}^{16}\text{O}}}$$

$$= \frac{m_{^{13}\text{C}} m_{^{16}\text{O}}}{(m_{^{13}\text{C}} + m_{^{16}\text{O}})} \times \frac{(m_{^{12}\text{C}} + m_{^{16}\text{O}})}{m_{^{12}\text{C}} m_{^{16}\text{O}}}$$

$$= \frac{m_{^{13}\text{C}}(m_{^{12}\text{C}} + m_{^{16}\text{O}})}{m_{^{12}\text{C}}(m_{^{13}\text{C}} + m_{^{16}\text{O}})} = \frac{M_{^{13}\text{C}}(M_{^{12}\text{C}} + M_{^{16}\text{O}})}{M_{^{12}\text{C}}(M_{^{13}\text{C}} + M_{^{16}\text{O}})}$$

### Effect of Isotopic Substitution

### Example 4.4.1

### Solution

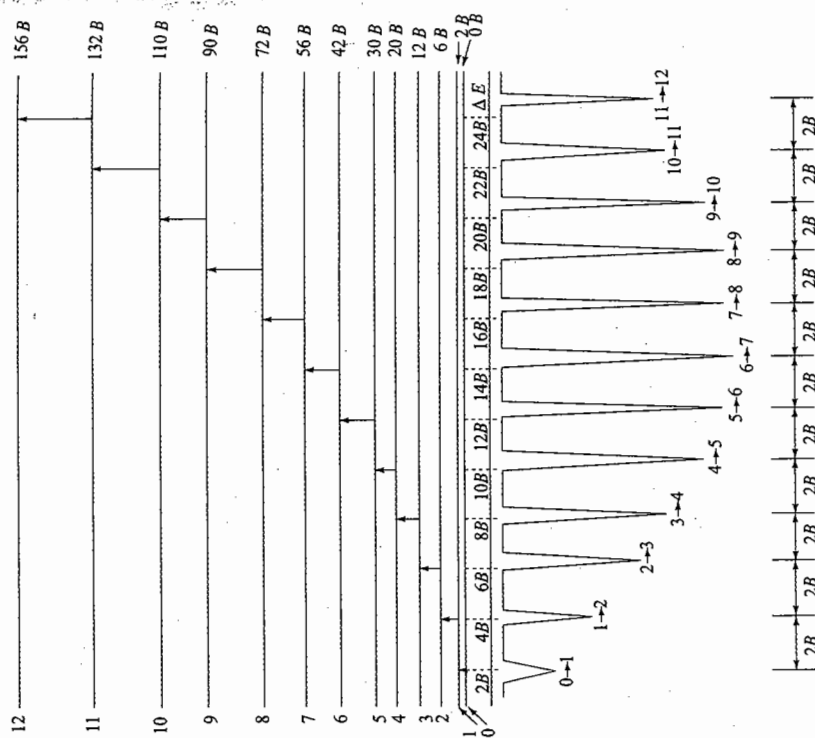


Fig. 4.4.5 A typical rotational spectrum

The rotational spectrum can be used to determine the bond distance of a diatomic molecule. Take, for example, the case of CO molecule; the first line in the spectrum is found to be at  $3.8424 \text{ cm}^{-1}$ . This is equal to  $2B$ . Thus, we have

$$\begin{aligned}\tilde{\nu}_J = 1 \leftarrow J'' = 0 = 2B &= 3.8424 \text{ cm}^{-1} \\ \text{Thus } B &= 1.9212 \text{ cm}^{-1} = 1.9212 \times 10^2 \text{ m}^{-1}\end{aligned}$$

$$\text{Since } B = \frac{h}{8\pi^2 Ic} \quad \text{therefore } I = \frac{h}{8\pi^2 Bc}$$

Substituting the values, we have

$$\begin{aligned}I &= \frac{(6.626 \times 10^{-34} \text{ J s})}{8(3.14)^2 (1.9212 \times 10^2 \text{ m}^{-1})(2.998 \times 10^8 \text{ m s}^{-1})} \\ &= 1.458 \times 10^{-46} \text{ kg m}^2\end{aligned}$$

$$\text{Now } I = \mu r^2 \quad \text{therefore } r = (I/\mu)^{1/2}$$

$$\text{Thus } \frac{1.9212 \text{ cm}^{-1}}{18367 \text{ cm}^{-1}} = \frac{M_{13} (12.0000 + 15.9994)}{(12.0000)(M_{13} + 15.9994 \text{ g mol}^{-1})}$$

Solving for  $M_{13}$ , we get

$$M_{13} = 13.0007 \text{ g mol}^{-1}$$

### Example 4.4.2

The wavenumbers of pure rotational lines of HBr are represented by the equation  $\tilde{\nu} = (16.90 \text{ J cm}^{-1})$ , where  $J$  has integral values. Calculate: (a) The moment of inertia, (b) The internuclear distance of HBr, (c) Rotational frequency and the period of rotation for the rotational quantum number 1, (d) Which rotational energy level has the highest population at 298 K? (e) What is the change in rotational constant when H is replaced by D?

(a) The difference between the two successive energy levels as given by Eq. (4.4.16) is

$$\Delta \tilde{E} = 2B(J'' + 1) = 2B(J')$$

Equating this to the given value, we get

$$2B = 16.90 \text{ cm}^{-1}$$

$$\text{or } B = 8.45 \text{ cm}^{-1} = 8.45 \times 10^2 \text{ m}^{-1}$$

Now  $B$  is given by

$$B = \frac{h}{8\pi^2 I c}$$

$$\text{Hence } I = \frac{h}{8\pi^2 B c} = \frac{(6.626 \times 10^{-34} \text{ J s})}{8\pi^2 (8.45 \times 10^2 \text{ m}^{-1})(2.998 \times 10^8 \text{ m s}^{-1})}$$

$$= 3.316 \times 10^{-47} \text{ J s}^2 = 3.316 \times 10^{-47} \text{ kg m}^2$$

(b) Now

$$I = \mu r^2$$

where  $\mu$  for HBr is

$$\mu_{\text{HBr}} = \frac{m_{\text{H}} m_{\text{Br}}}{m_{\text{H}} + m_{\text{Br}}} = \frac{((0.001 \text{ kg})/(6.023 \times 10^{23}))((0.0799 \text{ kg})/(6.023 \times 10^{23}))}{(0.001 \text{ kg})/(6.023 \times 10^{23}) + ((0.0799 \text{ kg})/(6.023 \times 10^{23}))} = 1.64 \times 10^{-27} \text{ kg}$$

Thus

$$r = \sqrt{\frac{I}{\mu}} = \left( \frac{3.316 \times 10^{-47} \text{ kg m}^2}{1.64 \times 10^{-27} \text{ kg}} \right)^{1/2} = 1.42 \times 10^{-10} \text{ m} = 142 \text{ pm}$$

(c) The energy of the rotational level for  $J = 1$  will be

$$\tilde{E}_1 = 16.90 \text{ cm}^{-1} = 16.90 \times 10^2 \text{ m}^{-1}$$

Converting this to the joule unit, we have

$$\tilde{E}_1 = hc \tilde{E} = (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})(16.90 \times 10^2 \text{ m}^{-1}) = 3.357 \times 10^{-22} \text{ J}$$

From classical mechanics, the kinetic energy  $E_k$  of the molecule is given by

$$E_k = \frac{1}{2} I \omega^2$$

where  $\omega$  is the angular velocity in radians per second.

Hence

$$\omega = \sqrt{\frac{2E_k}{I}} = \left( \frac{2 \times 3.357 \times 10^{-22} \text{ J}}{3.316 \times 10^{-47} \text{ kg m}^2} \right)^{1/2} = 4.50 \times 10^{12} \text{ s}^{-1}$$

Now  $\omega = 2\pi\nu$ , where  $\nu$  is the frequency of rotation. Hence

$$\nu = \frac{\omega}{2\pi} = \frac{4.50 \times 10^{12} \text{ s}^{-1}}{2 \times 3.14} = 7.169 \times 10^{11} \text{ s}^{-1}$$

Period of rotation,  $\tau = 1/\nu = 1.395 \times 10^{-12} \text{ s}$

(d) The rotational level having maximum population is given by the quantum number

$$J = \sqrt{\frac{1}{2} \frac{kT}{Bc} - \frac{1}{2}} = \left\{ \frac{1}{2} \frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{(8.45 \times 10^2 \text{ m}^{-1})(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})} \right\}^{1/2} - \frac{1}{2} = 3.5 - 0.5 = 3$$

(e) The substitution of H by D does not affect the internuclear distance of HBr but changes only its reduced mass. Since  $B$  is inversely related to  $I$ , we may write

$$\frac{B_{\text{DBr}}}{B_{\text{HBr}}} = \frac{\mu_{\text{HBr}}}{\mu_{\text{DBr}}}$$

$$\text{But } \mu_{\text{DBr}} = \frac{m_{\text{D}} m_{\text{Br}}}{m_{\text{D}} + m_{\text{Br}}} = \frac{((0.002 \text{ kg})/(6.023 \times 10^{23}))((0.0799 \text{ kg})/(6.023 \times 10^{23}))}{(0.002 \text{ kg})/(6.023 \times 10^{23}) + ((0.0799 \text{ kg})/(6.023 \times 10^{23}))} = 3.239 \times 10^{-27} \text{ kg}$$

$$\text{Hence } B_{\text{DBr}} = \left( \frac{1.64 \times 10^{-27} \text{ kg}}{3.239 \times 10^{-27} \text{ kg}} \right) (8.45 \text{ cm}^{-1}) = 4.278 \text{ cm}^{-1}$$

(a) Show that the frequency of rotation ( $\text{s}^{-1}$ ) of a rigid rotator increases with increase in rotational quantum number  $J$  according to the expression

$$\nu = \frac{h}{4\pi^2 I} \sqrt{J(J+1)}$$

(b) The increase in the frequency of rotation increases the centrifugal force which tends to move the atoms apart. Consequently, the bond length of a diatomic molecule increases with increase in the value of  $J$ , i.e. the molecule does not behave as a rigid rotator but as a nonrigid rotator. For a molecule executing simple harmonic motion and behaving like a nonrigid rotator, the wavenumber of the rotational level is given by the expression

$$\tilde{E}_J = B J(J+1) - D J^2(J+1)^2$$

where  $D$  is known as centrifugal distortion constant and is given by the expression

$$D = \frac{h^3}{32\pi^4 I^2 r^2 k_t c} = \frac{16B^3 \pi^2 \mu c^2}{k_t}$$

where  $k_t$  is the force constant of the bond (see Section 4.5). Show that for such a molecule, the difference between two nearest rotational levels is given by the relation

$$\Delta \tilde{E}_{J+1 \leftarrow J} = \tilde{\nu}_J = 2(J+1) \{B - 2D(J+1)^2\}$$

and hence conclude that  $\Delta \tilde{E}_{J+1 \leftarrow J}$  decreases with increase in the value of  $J$ .

(c) Three consecutive lines in the rotational spectrum of  $\text{H}^{79}\text{Br}$  are observed at 84,544, 101,355 and  $118,112 \text{ cm}^{-1}$ . Assign the lines to their appropriate  $J' \leftarrow J''$  transitions, then deduce values for  $B$  and  $D$  and hence evaluate the bond length and approximate values of force constant and vibrational frequency of the molecule.

(a) The energy expression for the rotational levels of a rigid rotator is given by

$$E = \frac{h^2}{8\pi^2 I} J(J+1) \quad (1)$$

According to classical mechanics, the kinetic energy of the molecule is given by

$$E_k = \frac{1}{2} I \omega^2$$

where  $\omega$  is the angular velocity in radians per second. Since

$$\omega = 2\pi\nu$$

we have

$$E_k = \frac{1}{2} I (2\pi\nu)^2 = 2I\pi^2\nu^2 \quad (2)$$

Equating Eqs (1) and (2), we get

$$2I\pi^2\nu^2 = \frac{h^2}{8\pi^2 I} J(J+1)$$

or

$$\nu = \frac{h}{4\pi^2 I} \sqrt{J(J+1)}$$

$$(b) \quad \Delta \tilde{E}_{J+1 \leftarrow J} = \tilde{E}_{J+1} - \tilde{E}_J$$

$$\begin{aligned} &= \{B(J+1)(J+2) - D(J+1)^2(J+2)^2\} - \{BJ(J+1) - DJ^2(J+1)^2\} \\ &= 2B(J+1) - 4D(J+1)^3 \\ &= 2(J+1) \{B - 2D(J+1)^2\} \end{aligned}$$

As  $J$  increases, the factor  $B - 2D(J+1)^2$  decreases and hence  $\Delta \tilde{E}_{J+1 \leftarrow J}$  decreases with increase in the value of  $J$ .

(c) The difference between the given transitions is of the order of  $17 \text{ cm}^{-1}$ . For a rigid rotator, this difference is  $2B$ . Hence, the first transition at  $84,544 \text{ cm}^{-1}$  will be of the order of  $10B$ . The latter value corresponds to  $J' = 5 \leftarrow J'' = 4$  transition for a rigid rotator and hence we conclude the following rotational transitions in  $\text{H}^{79}\text{Br}$  molecule.

$$\tilde{E}_{J'=5 \leftarrow J''=4} = 84,544 \text{ cm}^{-1}$$

$$\tilde{E}_{J'=6 \leftarrow J''=5} = 101,355 \text{ cm}^{-1}$$

$$\tilde{E}_{J'=7 \leftarrow J''=6} = 118,112 \text{ cm}^{-1}$$

Employing the relation given in Part (b), we get

$$84,544 \text{ cm}^{-1} = 2(5) \{B - 2D(25)\}$$

$$101,355 \text{ cm}^{-1} = 2(6) \{B - 2D(36)\}$$

Solving for  $B$  and  $D$ , we get

$$B = 8,473 \text{ cm}^{-1}$$

$$D = 3.704 \times 10^{-4} \text{ cm}^{-1}$$

$$\text{Now since } B = \frac{h}{8\pi^2 I c}, \text{ we get } I = \frac{h}{8\pi^2 B c}$$

Substituting the values, we get

$$I = \frac{(6.626 \times 10^{-34} \text{ J s})}{8(22/7)^2 (8,473 \times 10^2 \text{ m}^{-1}) (2.998 \times 10^8 \text{ m s}^{-1})}$$

$$= 3.301 \times 10^{-47} \text{ kg m}^2$$

$$\text{Now } I = \mu r^2$$

$$\text{where } \mu = \frac{m_{\text{H}} m_{\text{Br}}}{m_{\text{H}} + m_{\text{Br}}}$$

$$\begin{aligned} &= \frac{\{(0.001 \text{ kg})/(6.023 \times 10^{23})\} \{(0.0799 \text{ kg})/(6.023 \times 10^{23})\}}{\{(0.001 \text{ kg})/(6.023 \times 10^{23})\} + \{(0.0799 \text{ kg})/(6.023 \times 10^{23})\}} \\ &= 1.64 \times 10^{-27} \text{ kg} \end{aligned}$$

$$\text{Hence } r = \sqrt{\frac{I}{\mu}} = \left( \frac{3.301 \times 10^{-47} \text{ kg m}^2}{1.64 \times 10^{-27} \text{ kg}} \right)^{1/2} = 1.419 \times 10^{-10} \text{ m} = 141.9 \text{ pm}$$

$$\text{Since } D = \frac{16B^3 \pi^2 \mu c^2}{k_t}, \text{ we have}$$

$$k_t = \frac{16B^3 \pi^2 \mu c^2}{D}$$

$$= \frac{16(8,473 \times 10^2 \text{ m}^{-1})^3 (22/7)^2 (1.64 \times 10^{-27} \text{ kg}) (2.998 \times 10^8 \text{ m s}^{-1})^2}{(3.704 \times 10^{-4} \text{ m}^{-1})}$$

$$= 3.825 \times 10^2 \text{ N m}^{-1}$$

$$\begin{aligned} \nu &= \frac{1}{2\pi} \sqrt{\frac{k_t}{\mu}} = \frac{1}{2(22/7)} \sqrt{\frac{3.825 \times 10^2 \text{ N m}^{-1}}{1.64 \times 10^{-27} \text{ kg}}} \\ &= 7.68 \times 10^{13} \text{ s}^{-1} \end{aligned}$$





## 4.5 VIBRATIONAL SPECTRA OF DIATOMIC MOLECULES

### Introduction

The absorption spectrum in the infrared region corresponds to the promotion of a molecule from its lowest vibrational level to the next higher one. The correlation of experimental absorption with the theoretical difference in energy levels yields information on the flexibility of the bond undergoing the vibrational motion. By flexibility, we mean the relative easiness with which the bond length and bond angle of the molecule can be distorted from the equilibrium configuration.

### Classical Frequency of Harmonic Oscillator

Figure 4.5.1 illustrates the typical vibration exhibited by a diatomic molecule.

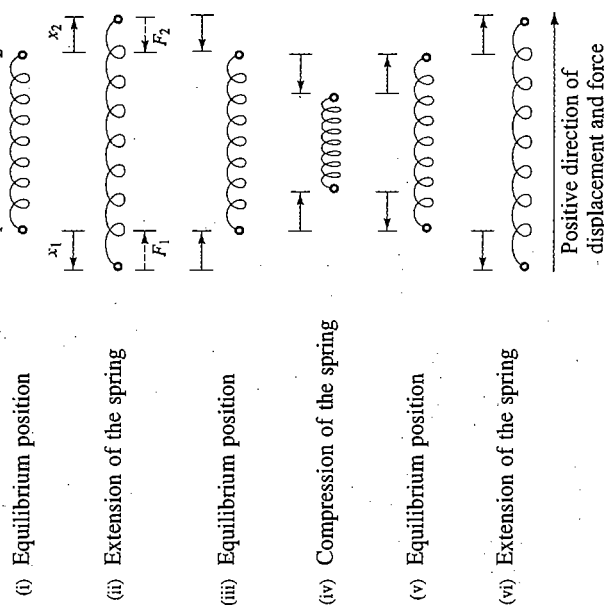


Fig. 4.5.1 Symmetrical stretching vibration of a diatomic molecule

Solid arrows indicate the directions of motion of atoms and dotted arrows indicate the directions of restoring forces.

The vibration shown in Fig. 4.5.1 is known as the *symmetrical stretching vibration*. In classical mechanics, this vibration may be represented by a model in which two balls of masses  $m_1$  and  $m_2$  are connected with each other by a spring. To determine the displacement of the ball from its equilibrium position and the force acting on it, we choose the axis system as shown in Fig. 4.5.1. Thus, the displacement to the right of the equilibrium position will have a positive value whereas that to the left has a negative value.

A harmonic oscillator follows Hooke's law, according to which, the restoring force  $F$  acting on the ball is directly proportional to the displacement  $\Delta x$ , i.e.

$$F = -k_f(\Delta x) \quad (4.5.1)$$

where  $k_f$  is a constant, known as the *force constant*. This constant is a characteristic constant of the spring and is a measure of the stiffness of the spring (or the bond). The negative sign in Eq. (4.5.1) indicates that the force is a restoring force and thus has a direction opposite to that of the displacement.

Let  $x_1$  and  $x_2$  be the displacements of the two balls as shown in Fig. 4.5.1. Then, we have

$$\text{Extension of the spring} = x_2 - x_1 \quad (4.5.2)$$

According to the Newton's second law, we have

$$\text{Restoring force acting on the ball 1} = m_1 \frac{d^2 x_1}{dt^2} \quad (4.5.3)$$

$$\text{Restoring force acting on the ball 2} = m_2 \frac{d^2 x_2}{dt^2} \quad (4.5.4)$$

Now, according to Hooke's law and the sign convention shown in Fig. 4.5.1, we have

$$\text{Restoring force acting on the ball 1} = k_f(x_2 - x_1) \quad (4.5.5)$$

$$\text{Restoring force acting on the ball 2} = -k_f(x_2 - x_1) \quad (4.5.6)$$

From Eqs (4.5.3) and (4.5.5), and Eqs (4.5.4) and (4.5.6), we get

$$m_1 \frac{d^2 x_1}{dt^2} = k_f(x_2 - x_1) \quad (4.5.7a)$$

$$m_2 \frac{d^2 x_2}{dt^2} = -k_f(x_2 - x_1) \quad (4.5.7b)$$

The coordinates  $x_1$  and  $x_2$  follow either the cosine or sine relation given below.

$$x_1 = A_1 \cos(2\pi\nu t) \quad \text{or} \quad x_1 = A_1 \sin(2\pi\nu t) \quad (4.5.8)$$

$$x_2 = A_2 \cos(2\pi\nu t) \quad \text{or} \quad x_2 = A_2 \sin(2\pi\nu t) \quad (4.5.9)$$

where  $A_1$  and  $A_2$  are the amplitudes of the vibrations of balls 1 and 2, respectively, and  $\nu$  is the frequency of vibration. The term  $1/\nu$  gives the time interval required for the balls to complete one vibration. Note that  $A_1$  and  $A_2$  may have different values but the frequency  $\nu$  has the same value for both the balls.

Substituting the cosine relations (we can equally use the sine functions) in Eqs (4.5.7a) and (4.5.7b), we get

$$m_1 \frac{d^2 A_1 \cos(2\pi\nu t)}{dt^2} = k_f(A_2 - A_1) \cos(2\pi\nu t)$$

$$m_2 \frac{d^2 A_2 \cos(2\pi\nu t)}{dt^2} = -k_f(A_2 - A_1) \cos(2\pi\nu t)$$

On carrying out the differentiations and cancelling the common terms, we get

$$-m_1 A_1 (2\pi\nu)^2 = k_f(A_2 - A_1)$$

$$-m_2 A_2 (2\pi\nu)^2 = -k_f(A_2 - A_1)$$

Writing the above equations in the determinant form, we get

$$\begin{vmatrix} m_1(2\pi\nu)^2 - k_f & k_f \\ k_f & m_2(2\pi\nu)^2 - k_f \end{vmatrix} \begin{vmatrix} A_1 \\ A_2 \end{vmatrix} = 0$$

In order to have nontrivial roots of  $A_1$  and  $A_2$ , we must have

$$\begin{vmatrix} m_1(2\pi\nu)^2 - k_f & k_f \\ k_f & m_2(2\pi\nu)^2 - k_f \end{vmatrix} = 0$$

Opening this determinant, we get

$$m_1 m_2 (2\pi\nu)^4 - k_f m_1 (2\pi\nu)^2 - k_f m_2 (2\pi\nu)^2 + k_f^2 - k_f^2 = 0$$

$$\text{or } m_1 m_2 (2\pi\nu)^2 - k_f (m_1 + m_2) = 0$$

$$\text{or } \nu = \frac{1}{2\pi} \sqrt{\frac{k_f}{m_1 m_2 / (m_1 + m_2)}} = \frac{1}{2\pi} \sqrt{\frac{k_f}{\mu}} \quad (4.5.10)$$

where  $\mu = m_1 m_2 / (m_1 + m_2)$  and is known as the reduced mass of the molecule.

Equation (4.5.10) is the required characteristic frequency at which atoms of a diatomic molecule undergo harmonic vibration.

### Classical Potential Energy of Harmonic Vibration of a Diatomic Molecule

The potential energy of a system at any instant can be evaluated from the expression

$$F = - \frac{dV}{dx} \quad (4.5.11)$$

In the present case, we have

$$-k_f \Delta x = - \frac{dV}{d(\Delta x)}$$

$$\text{or } dV = k_f \Delta x d(\Delta x)$$

On integrating, we get

$$V = k_f \frac{(\Delta x)^2}{2} + I$$

where  $I$  is the constant of integration whose value may be determined from the fact that at  $\Delta x = 0$ ,  $V = 0$ . Thus  $I = 0$  and the potential energy expression becomes

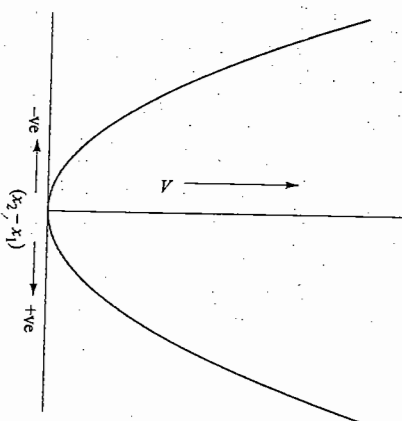
$$V = \frac{1}{2} k_f (\Delta x)^2 \quad (4.5.12)$$

The variation of potential energy with displacement is shown in Fig. 4.5.2. Classically speaking, the molecule can vibrate with any amount of potential energy, i.e. the potential energy of the molecule is a continuous function of the displacement from the equilibrium position.

The vibrational motion of a real diatomic molecule is approximately harmonic for a small displacement near the equilibrium internuclear configuration (see Fig. 4.5.5). Thus, from Eq. (4.5.12) it follows that for a real diatomic molecule

$$k_f = \left( \frac{\partial^2 V}{\partial (\Delta x)^2} \right)_{\Delta x \rightarrow 0}$$

Fig. 4.5.2 Potential energy diagram for a classical oscillator



that is, the force constant is equal to the value of second derivative of potential energy  $V$  with respect to the displacement  $\Delta x$  evaluated when  $\Delta x$  approaches zero. In other words, it is a measure of rate of change of the slope of  $V$  versus  $\Delta x$  graph near the equilibrium internuclear configuration, i.e. it is a measure of the curvature of the potential well near the equilibrium internuclear configuration.

Since the classical laws do not hold good for particles of very small masses, Eq. (4.5.12) will not be applicable to diatomic molecules. The potential energy expression for such a case has to be derived quantum mechanically by solving the appropriate Schrödinger equation. In the present case the solution of Schrödinger equation yields the following expression of potential energy:

$$V_v = \left( v + \frac{1}{2} \right) h\nu_{\text{classical}} \quad (4.5.13)^{\dagger}$$

where  $\nu_{\text{classical}}$  is the classical frequency of vibration (Eq. 4.5.10) and  $v$  is the vibrational quantum number. The allowed values of the latter are 0, 1, 2, ..., etc. Thus, the vibrational energies are quantized, i.e. the molecule cannot vibrate with any arbitrary amount of energy but with only certain discrete vibrational energies as given by Eq. (4.5.13).

The allowed vibrational energy levels of a diatomic molecule are shown by the horizontal lines within the classical potential energy diagram (Fig. 4.5.2). The following two characteristics may be noted down.

- The energy levels are equally spaced, i.e. the difference between the two nearest levels is the same throughout and has a value of  $h\nu_{\text{classical}}$ .

If  $v$  and  $(v+1)$  are the vibrational quantum numbers of the two nearest energy levels, we have

$$\Delta V = \{ (v+1) + 1/2 \} h\nu_{\text{classical}} - \{ v + 1/2 \} h\nu_{\text{classical}} = h\nu_{\text{classical}} \quad (4.5.14)$$

<sup>†</sup> The vibrational energy expressed in wavenumber unit is known as vibration term (symbol:  $G$ ), i.e.  $G = V/hc$ .

- The lowest vibrational energy ( $\nu = 0$ ) is not zero as in the case of classical vibrator but has a value of  $(1/2)h\nu_{\text{classical}}$ .

This lowest energy is known as *zero-point energy*. This means that the atoms in a molecule can never be completely at rest relative to each other. This fact is in agreement with the Heisenberg uncertainty principle. If the atoms were standstill the uncertainty in the position would be zero and hence, according to the uncertainty principle, the uncertainty in the momentum would have been infinite. In order to avoid this, the atoms ought to have certain uncertainty in position, i.e. the atoms will have to have some vibrational energy.

In classical mechanics, the minimum vibrational energy which a diatomic molecule can possess is zero, i.e. the atoms can be at rest relative to each other.

The zero-point energy is just half of the energy difference between the two nearest vibrational energy levels. It may be noted that both these quantities depend on the classical vibration frequency and hence on the strength of the chemical bond and the atomic masses (Eq. 4.5.10).

The relative populations of energy levels as given by Boltzmann equation is

$$N_i = N_0 \exp(-\Delta E_i/kT)$$

where  $\Delta E_i$  the energy difference between the  $i$ th level and the zeroeth level. The relative population, i.e. the term  $N_i/N_0$ , depends on the ratio  $\Delta E_i/kT$ . From the experimental data on the vibrational spectra, it is found that in most diatomic molecules  $\Delta E_{1 \leftarrow 0}$  is much higher than the thermal energy  $kT$ . For example, for CO and  $\text{Cl}_2$  molecules we have

$$\begin{array}{l} \text{Carbon monoxide} \quad \Delta E_{1 \leftarrow 0} = 42 \times 10^{-21} \text{ J} \\ \text{Chlorine} \quad \Delta E_{1 \leftarrow 0} = 11 \times 10^{-21} \text{ J} \end{array}$$

These values may be compared with the thermal energy  $4.1 \times 10^{-21} \text{ J}$  at 298 K. On computing the ratios  $N_1/N_0$ ,  $N_2/N_0$  for these molecules, we find that

For carbon monoxide

$$\begin{aligned} \frac{N_1}{N_0} &= \exp\{(-42 \times 10^{-21} \text{ J})/(4.1 \times 10^{-21} \text{ J})\} = \exp(-10.244) = 3.6 \times 10^{-5} \\ \frac{N_2}{N_0} &= \exp\{(-84 \times 10^{-21} \text{ J})/(4.1 \times 10^{-21} \text{ J})\} = \exp(-20.488) = 3.1 \times 10^{-9} \end{aligned}$$

For chlorine

$$\begin{aligned} \frac{N_1}{N_0} &= \exp\{(-11 \times 10^{-21} \text{ J})/(4.1 \times 10^{-21} \text{ J})\} = \exp(-2.683) = 6.8 \times 10^{-2} \\ \frac{N_2}{N_0} &= \exp\{(-22 \times 10^{-21} \text{ J})/(4.1 \times 10^{-21} \text{ J})\} = \exp(-5.366) = 4.7 \times 10^{-3} \end{aligned}$$

From the above calculated values, we observe that the populations in the higher vibrational levels are negligible in comparison to the population in the ground level. Thus, we may conclude that the excitation of molecules from  $\nu = 0$  level will be much more intense than from any of the higher levels.

### Mechanism of interaction with Radiation

The interaction between the radiation and the vibrating molecule is through the fluctuating electric field of the radiation and the similar field generated by the vibration of the molecule. The electrical component of the radiation oscillates in a plane perpendicular to the direction of propagation of the wave. The frequency of this oscillating electrical component is equal to the frequency of the radiation. On the other hand, an oscillating electrical field from a molecule is generated only when there occurs a *change in dipole moment* during the vibration of the molecule.

In diatomic molecules, we have only one type of vibration, i.e. symmetrical stretching vibration, where the molecule is alternately stretched and compressed. It is expected that the change in dipole moment during the vibration of a diatomic molecule will occur only if the molecule has a permanent dipole moment. This is shown in Fig. 4.5.3.

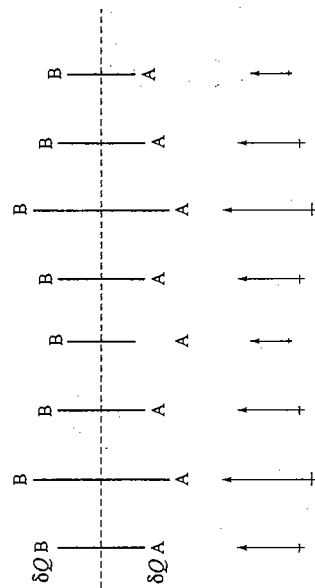


Fig. 4.5.3 The vibration of dipole moment during the stretching vibration of diatomic molecule having permanent dipole moment

Homonuclear diatomic molecules have zero dipole moment and also there occurs no change in dipole moment during the symmetrical stretching vibration, and hence such molecules are *infrared inactive*, i.e. they do not show any vibrational spectra. Heteronuclear diatomic molecules do have a permanent dipole moment and they also exhibit a change in dipole moment during the vibration and hence are *infrared active*.

The active and inactive vibration modes of linear and nonlinear triatomic molecules may be illustrated here. We take the examples of  $\text{CO}_2$  (linear) and  $\text{H}_2\text{O}$  (nonlinear). It will be shown in Section 4.7 that the linear triatomic molecules have four fundamental vibration modes and nonlinear molecules have three fundamental vibration modes as described in Table 4.5.1.

Table 4.5.1 Vibrational Modes in a Triatomic Molecule

Vibrational mode	Description
1. Symmetrical stretch mode	Bonds are alternately stretched and compressed in a symmetrical manner
2. Antisymmetrical stretch mode	One bond is stretched while the other is compressed and vice versa
3. Bending mode (doubly degenerate for linear molecules)	Bond angle changes periodically within a plane

The changes in dipole moment during the three vibrational modes of  $\text{CO}_2$  are shown in Fig. 4.5.4.

From Fig. 4.5.4, it is obvious that the symmetrical stretching vibration will be infrared inactive whereas antisymmetrical and bending modes will be infrared active.

For water molecule, all the three vibrational modes will be infrared active as they are accompanied by the change in the dipole moment.

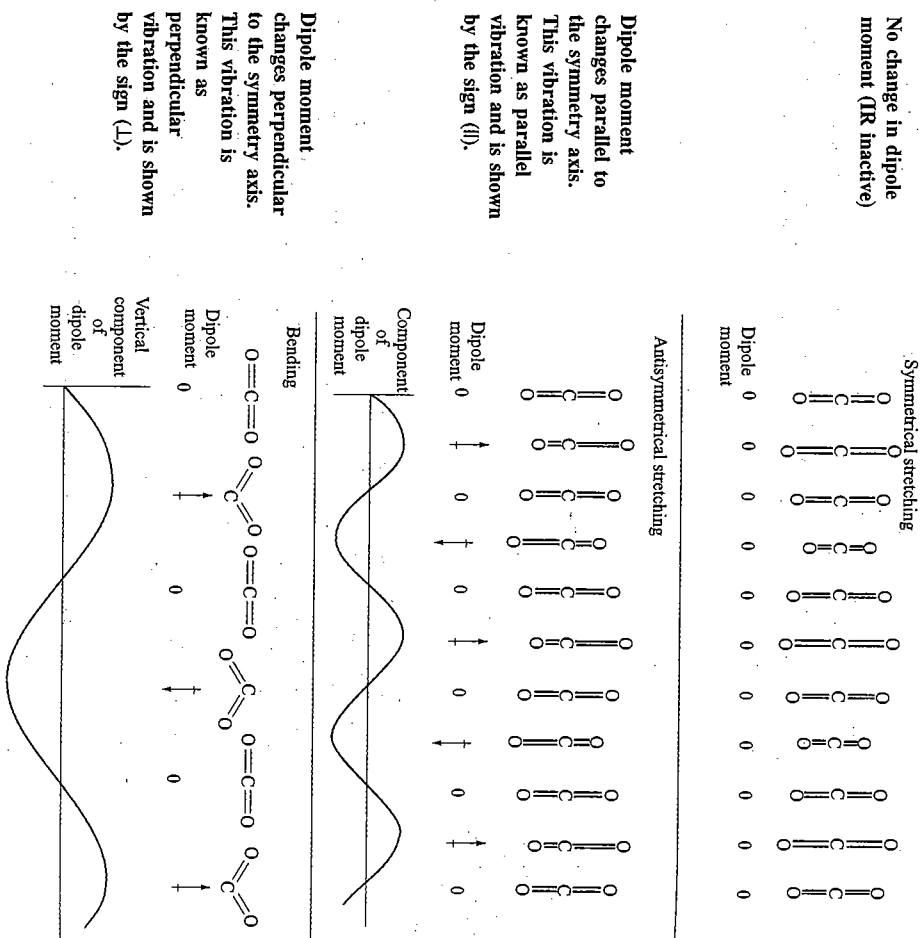


Fig. 4.5.4 The variations of dipole moment during the three vibrational motions of  $\text{CO}_2$

### Selection Rule

The quantum mechanical calculations show that for harmonic vibration of a heteronuclear diatomic molecule, the transition from one vibrational level to another occurs with the condition of

$$\Delta v = \pm 1 \quad (4.5.15)$$

that is, the change in the vibrational quantum number is unity. Equation (4.5.15) is, in fact, the selection rule for the vibrational transitions (see Section 4.1).

### Vibrational Spectrum

#### Determination of Force Constant

Since the vibrational levels are equally spaced (Eq. 4.5.14), transitions between any two neighbouring levels will give rise to the same energy change. Thus, only one absorption line is observed in the vibrational spectrum of a diatomic molecule.

Substituting Eq. (4.5.10) in Eq. (4.5.14), we get

$$\Delta v = \frac{h}{2\pi} \sqrt{\frac{k_f}{\mu}} \quad (4.5.16a)$$

which on rearranging gives

$$k_f = \frac{4\pi^2 \mu (\Delta v)^2}{h^2} \quad (4.5.16b)$$

Expressing  $\Delta v$  in the wavenumber unit, we have

$$\Delta \tilde{v} = \frac{\Delta v}{hc} = \frac{1}{2\pi c} \sqrt{\frac{k_f}{\mu}} \quad (4.5.17a)$$

On rearranging the above expression, we get

$$k_f = 4\pi^2 c^2 \mu (\Delta \tilde{v})^2 \quad (4.5.17b)$$

Equations (4.5.16b) and (4.5.17b) may be used to determine the force constant of a diatomic molecule.

For HCl and CO, the values of  $k_f$  have been calculated in the following.

**Hydrogen Chloride** From experiment, we find that

$$\Delta \tilde{v} = 2890 \text{ cm}^{-1} = 2890 \times 10^2 \text{ m}^{-1}$$

The value of  $\mu$  is

$$\begin{aligned} \mu &= \frac{m_{\text{H}} m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} = \frac{\{(0.001 \text{ kg}) / (6.023 \times 10^{23})\} \{(0.0355 \text{ kg}) / (6.023 \times 10^{23})\}}{\{(0.001 \text{ kg}) / (6.023 \times 10^{23})\} + \{(0.0355 \text{ kg}) / (6.023 \times 10^{23})\}} \\ &= 1.615 \times 10^{-27} \text{ kg} \end{aligned}$$

Hence  $k_f = 4\pi^2 c^2 \mu (\Delta \tilde{v})^2$

$$\begin{aligned} &= (4.314)^2 (2.998 \times 10^8 \text{ m s}^{-1})^2 (1.615 \times 10^{-27} \text{ kg}) (2890 \times 10^2 \text{ m}^{-1})^2 \\ &= 4.781 \times 10^2 \text{ kg s}^{-2} \approx 4.781 \times 10^2 \text{ N m}^{-1} \end{aligned}$$

**Carbon Monoxide** From experiment, we find that

$$\Delta v = 4.24 \times 10^{-20} \text{ J}$$

The value of  $\mu$  is

$$\begin{aligned} \mu &= \frac{m_{\text{C}} m_{\text{O}}}{m_{\text{C}} + m_{\text{O}}} = \frac{\{(0.012 \text{ kg}) / (6.023 \times 10^{23})\} \{(0.016 \text{ kg}) / (6.023 \times 10^{23})\}}{\{(0.012 \text{ kg}) / (6.023 \times 10^{23})\} + \{(0.016 \text{ kg}) / (6.023 \times 10^{23})\}} \\ &= 1.138 \times 10^{-26} \text{ kg} \end{aligned}$$

$$\text{Hence } k_f = \frac{4\pi^2 \mu (\Delta v)^2}{h^2} = \frac{4(3.14)^2 (1.138 \times 10^{-26} \text{ kg}) (4.24 \times 10^{-20} \text{ J})^2}{(6.626 \times 10^{-34} \text{ J s})^2}$$

$$= 1.838 \times 10^3 \text{ kg s}^{-2} \approx 1.838 \times 10^3 \text{ N m}^{-1}$$

### Amplitude of Vibration

Coming to the amplitude of vibration, we find from classical mechanics that at the extremes of vibration, whole of the energy is present in the form of potential energy. Equating the classical expression of potential energy  $(1/2)kx_{\max}^2$  with the vibrational energy, we can find the maximum displacement  $x_{\max}$  from the equilibrium bond length. Thus, we have

$$\frac{1}{2}k_f x_{\max}^2 = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \left( v + \frac{1}{2} \right) \quad (4.5.18)$$

$$\text{Hence } x_{\max} = \left\{ \frac{h}{\pi} \sqrt{\frac{1}{k_f \mu}} \left( v + \frac{1}{2} \right) \right\}^2 \quad (4.5.18)$$

Let us now compute the vibrational amplitude of HCl molecule in the lowest vibrational level, i.e.  $v = 0$ . From Eq. (4.5.18), we get

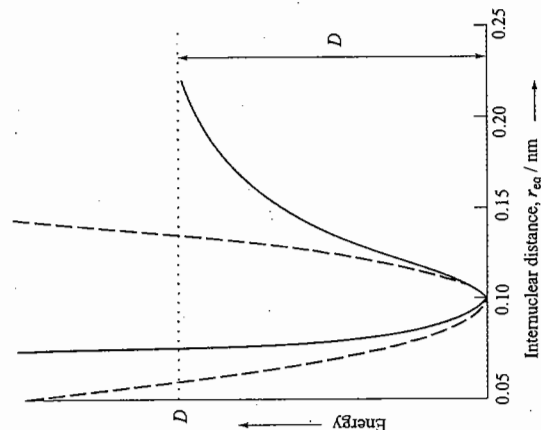
$$x_{\max} = \left( \frac{h}{2\pi} \sqrt{\frac{1}{k_f \mu}} \right)^{1/2} \left[ \frac{(6.626 \times 10^{-34} \text{ J s})}{(2 \times 3.14)} \left\{ \frac{1}{(4.781 \times 10^3 \text{ kg s}^{-2})(1.615 \times 10^{-27} \text{ kg})} \right\}^{1/2} \right] \\ = 1.096 \times 10^{-11} \text{ m} = 10.96 \text{ pm}$$

The equilibrium bond length of HCl is 127 pm. Thus, we find that the vibrational amplitude is about 10 per cent of the bond length. With such a small displacement, the vibration may be considered harmonic in nature.

The vibrational quantum number in the energy expression of a harmonic oscillator (Eq. 4.5.13) can have any value starting from the minimum value of zero to any larger integral value. This means that a diatomic molecule which is considered to execute harmonic oscillations can have any higher allowed energy without exhibiting any sign of breaking into two atoms. This fact is contrary to the experimental behaviour that the molecule breaks into atoms if it is stretched beyond a certain limit. Figure 4.5.5 compares the classical potential energy diagram of a harmonic oscillator with the actual energy diagram of a typical diatomic molecule. The two curves differ very widely in the lower and higher internuclear distances. The actual energy diagram rises more steeply than the harmonic parabola energy diagram in the lower internuclear distance. In the higher internuclear distance, the energy of harmonic oscillator goes on increasing without any limit whereas that in the actual energy diagram, the rise is less steep and it approaches the limiting dissociation energy at some finite internuclear distance. In the region near to the equilibrium internuclear distance, the two curves do not show appreciable departure from each other. This fact is in agreement with the statement made earlier that in the lowest vibrational level, the oscillation may be considered to be harmonic since the maximum displacement from the equilibrium bond length, which is about 10 per cent, is not very large. Within this displacement, the bond may be considered to be elastic so as to obey Hooke's law.

### Anharmonic Vibration

Fig. 4.5.5 Potential energy diagram of a real diatomic molecule (solid curve)



The maximum displacement from the equilibrium bond length increases with increase in vibrational quantum number (Eq. 4.5.18). For larger displacements, the bonds are no longer elastic and hence deviation from the harmonic vibration energy is expected for the larger vibrational quantum numbers.

### Morse Potential

Many empirical expressions have been suggested for the correlation of energy of a diatomic molecule with the internuclear distance. One of the expressions which fits the potential energy curve to a good approximation is due to P.M. Morse and is known as *Morse potential*. The energy expression is

$$V = D [1 - \exp\{a(r_{\text{eq}} - r)\}]^2 \quad (4.5.19)$$

where  $a$  is a constant for a particular molecule and  $D$  is the dissociation energy.

The constant  $a$  is given by  $\sqrt{k_f/2D}$  (see Example 4.5.5).

### Vibrational Energy of a Diatomic Molecule following the Morse Potential

Substitution of the Morse potential energy expression in Schrödinger equation and the approximate solution of the resultant equation gives the following energy expression for the various allowed vibrational potential energy levels.

$$V_v = (v + 1/2) \tilde{\nu}_e [1 - (v + 1/2)x_e] \quad (4.5.20a)$$

In the wavenumber unit we have

$$\tilde{V}_v = (v + 1/2) \tilde{\nu}_e [1 - (v + 1/2)x_e] \quad (4.5.20b)$$

where  $\tilde{\nu}_e$  is known as equilibrium oscillation frequency of the anharmonic oscillator,  $x_e$  is the corresponding anharmonicity constant and  $v$  is the vibrational quantum number which has integral values including zero, i.e.  $v = 0, 1, 2, \dots$ . The

anharmonicity constant  $x_e$  is approximately given by  $h\nu_e/4D$  (see Eq. 4.5.25) and has a small positive value of the order of 0.01.

The potential energy as given by Eq. (4.5.20) may be written in the form similar to that of a harmonic oscillator (i.e. Eq. 4.5.13), if we write Eq. (4.5.20) as

$$V = \left(v + \frac{1}{2}\right) h\nu_e \quad \text{where} \quad V = \nu_e \left[1 - \left(v + \frac{1}{2}\right)x_e\right]$$

The above expressions suggest that anharmonic oscillator may be treated like an oscillator whose oscillation frequency decreases steadily with increasing  $v$ . The potential energy of a few low vibrational levels are given below.

$$v = 0 \quad V_0 = \frac{1}{2} h\nu_e \left(1 - \frac{1}{2}x_e\right)$$

$$v = 1 \quad V_1 = \frac{3}{2} h\nu_e \left(1 - \frac{3}{2}x_e\right)$$

$$v = 2 \quad V_2 = \frac{5}{2} h\nu_e \left(1 - \frac{5}{2}x_e\right)$$

$$v = 3 \quad V_3 = \frac{7}{2} h\nu_e \left(1 - \frac{7}{2}x_e\right) \quad (4.5.21)$$

The difference between the two vibrational potential energy levels is

$$\Delta V = \left(v' + \frac{1}{2}\right) h\nu_e \left\{1 - \left(v' + \frac{1}{2}\right)x_e\right\} - \left(v'' + \frac{1}{2}\right) h\nu_e \left\{1 - \left(v'' + \frac{1}{2}\right)x_e\right\} \quad (4.5.22)$$

where  $v'$  and  $v''$  are the vibrational quantum numbers of the higher and lower levels, respectively.

For the two nearest levels, we will have

$$v' = v'' + 1$$

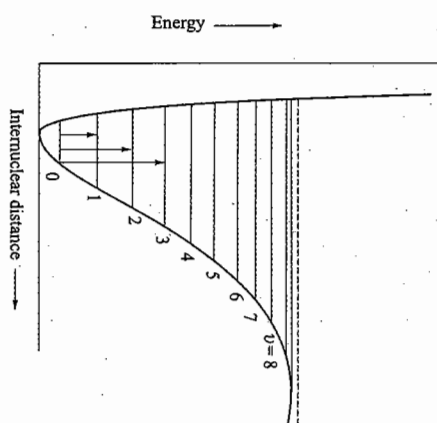
Hence, the potential energy difference between the two nearest levels is

$$\begin{aligned} \Delta V &= \left[\left(v'' + \frac{3}{2}\right) h\nu_e \left\{1 - \left(v'' + \frac{3}{2}\right)x_e\right\}\right] - \left[\left(v'' + \frac{1}{2}\right) h\nu_e \left\{1 - \left(v'' + \frac{1}{2}\right)x_e\right\}\right] \\ &= h\nu_e \{1 - 2x_e(1 + v'')\} \end{aligned} \quad (4.5.23)$$

Since the anharmonicity constant has a small positive value, it follows from Eq. (4.5.23) that the difference  $\Delta V$  between the two closest levels decreases with increasing value of vibrational quantum number. Thus, the vibrational levels are no more equally spaced as in the case of a harmonic oscillator but becomes closer to each other with increasing value of  $v$  (Fig. 4.5.6).

Fig. 4.5.6 The allowed energy levels (schematic of a diatomic molecule) executing anharmonic oscillations

### Vibrational Transitions



The selection rules for an anharmonic oscillator are

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots$$

Hence, all types of transitions from any lower vibrational level to any of the higher vibrational levels are allowed. Since only the lowest level is thickly populated and because the population decreases very rapidly with increasing  $v$ , only a few transitions from the lowest vibrational level ( $v = 0$ ) to the next nearest vibrational levels are actually observed at room temperature. The transition  $v' = 1 \leftarrow v'' = 0$  is found to be the most intense and is known as the *fundamental absorption*. The transition  $v' = 2 \leftarrow v'' = 0$ , is found to have a poor intensity and is known as the *first overtone*. The transition  $v' = 3 \leftarrow v'' = 0$  is found to have negligible intensity and is known as the *second overtone*. The higher overtones are too weak to be realized experimentally. The energies of the observed transitions may be worked out from Eq. (4.5.22) and are as follows:

$$(1) \quad v' = 1 \leftarrow v'' = 0; \quad \Delta V = h\nu_e (1 - 2x_e)$$

$$(2) \quad v' = 2 \leftarrow v'' = 0; \quad \Delta V = 2h\nu_e (1 - 3x_e)$$

$$(3) \quad v' = 3 \leftarrow v'' = 0; \quad \Delta V = 3h\nu_e (1 - 4x_e)$$

In the wave number unit, we have

$$(1) \quad v' = 1 \leftarrow v'' = 0; \quad \Delta \tilde{V} = \tilde{\nu}_e (1 - 2x_e)$$

$$(2) \quad v' = 2 \leftarrow v'' = 0; \quad \Delta \tilde{V} = 2\tilde{\nu}_e (1 - 3x_e)$$

$$(3) \quad v' = 3 \leftarrow v'' = 0; \quad \Delta \tilde{V} = 3\tilde{\nu}_e (1 - 4x_e)$$

The transitions from  $v = 1$  to the higher levels are not observed unless the temperature of the sample is high. This is due to the fact that the population in  $v = 1$  level is negligible at room temperature and it becomes appreciable at higher temperatures. These transitions are known as *hot bands* as they appear only at higher temperatures. The intensities of hot bands are usually very weak and become more intense on increasing temperature of the sample.

### Dissociation Energy of a Diatomic Molecule

The vibrational energy of a molecule increases with increase in the vibrational quantum number. Eventually, a stage is reached where vibrational energy is quite sufficient to break the molecule into atoms. This energy is known as the dissociation energy of the diatomic molecule. Thus at the dissociation stage of the molecule, the vibrational energy has a maximum value. The value of vibrational quantum number at this stage may be determined from Eq. (4.5.20a) by applying the mathematical criterion of maximum, i.e.  $\partial V/\partial v = 0$ . Thus, we have

$$\begin{aligned}\frac{\partial V}{\partial v} &= 0 = h\nu_e \left\{ 1 - (v_{\max} + 1/2)x_e \right\} + (v_{\max} + 1/2)h\nu_e (-x_e) \\ \text{or } 1 - 2(v_{\max} + 1/2)x_e &= 0 \\ \text{or } v_{\max} &= \frac{1}{2x_e} - \frac{1}{2}\end{aligned}\quad (4.5.24)$$

Substituting  $v_{\max}$  in Eq. (4.5.20a), we get

$$V_{\max} = \frac{h\nu_e}{4x_e} \quad (4.5.25)$$

This will represent the dissociation energy of the molecule with respect to the bottom of the potential energy diagram. The true dissociation energy, however, will be given by

$$\begin{aligned}D &= V_{\max} - V_0 \\ &= \frac{h\nu_e}{4x_e} - \frac{1}{2}h\nu_e \left( 1 - \frac{1}{2}x_e \right)\end{aligned}\quad (4.5.26)$$

The obtained value of dissociation energy will not be an accurate one since the energy expression (Eq. 4.5.20) is obtained as an approximate solution of the Schrödinger equation. More precise solution, in fact, includes the cubic, quartic, etc., terms in  $(v + 1/2)$  with anharmonicity constants  $y_e, z_e$ , etc. The magnitudes of  $y_e, z_e$ , etc., diminish very rapidly. Though these higher terms are negligible for the small values of  $v$ , they become important at large  $v$ .

### Example 4.5.1

The fundamental vibration frequency and rotational constant of CO molecule are  $6.5 \times 10^{13} \text{ s}^{-1}$  and  $1.743 \times 10^{11} \text{ s}^{-1}$ , respectively. Find the rotational quantum number for which the CO molecule will have the same energy as it would have in its first vibrational state with no rotational energy.

Since the rotational constant in terms of frequency unit is  $h/8\pi^2 I$ , we have

$$\frac{h}{8\pi^2 I} = 1.743 \times 10^{11} \text{ s}^{-1}$$

Thus, the expression of energy of various rotational levels is

$$\frac{E}{h} = \frac{h}{8\pi^2 I} J(J+1) = (1.743 \times 10^{11} \text{ s}^{-1}) J(J+1)$$

We have to calculate the value of  $J$  for which  $E/h$  is equal to the fundamental vibration frequency, i.e.  $6.5 \times 10^{13} \text{ s}^{-1}$ . Hence, we have

$$6.5 \times 10^{13} \text{ Hz} = (1.743 \times 10^{11} \text{ Hz}) J(J+1)$$

$$\text{or } J(J+1) = \frac{6.5 \times 10^{13}}{1.743 \times 10^{11}} = 372.9$$

Solving for  $J$ , we get

$$J = \frac{-1 + \sqrt{1 + 4 \times 372.9}}{2} = 18.82 \approx 19$$

### Example 4.5.2

The fundamental and first overtone transitions of  $^{14}\text{N}^{16}\text{O}$  are centred at  $1876.06 \text{ cm}^{-1}$  and  $3724.20 \text{ cm}^{-1}$ , respectively. Evaluate the equilibrium vibration frequency, the anharmonicity constant, the zero-point energy, the force constant and the dissociation energy of the molecule.

We have

$$\text{Fundamental absorption } \tilde{\nu}_e(1 - 2x_e) = 1876.06 \text{ cm}^{-1} \quad (i)$$

$$\text{First overtone } 2\tilde{\nu}_e(1 - 3x_e) = 3724.20 \text{ cm}^{-1} \quad (ii)$$

Dividing Eq. (ii) by Eq. (i), we get

$$\frac{2(1 - 3x_e)}{1 - 2x_e} = \frac{3724.20}{1876.06} = 1.985117$$

Solving for  $x_e$ , we get

$$x_e = 0.007332$$

Substituting the value of  $x_e$  in the expression

$$\tilde{\nu}_e(1 - 2x_e) = 1876.06 \text{ cm}^{-1}$$

and solving for  $\tilde{\nu}_e$ , we get

$$\tilde{\nu}_e = 1903.98 \text{ cm}^{-1}$$

The wavenumber corresponding to the zero-point energy for an anharmonic oscillator is given by

$$\begin{aligned}\tilde{E}_0 &= \frac{1}{2}\tilde{\nu}_e \left( 1 - \frac{1}{2}x_e \right) \\ &= \frac{1}{2}(1903.98 \text{ cm}^{-1}) \left( 1 - \frac{1}{2} \times 0.007332 \right) \\ &= 948.5 \text{ cm}^{-1}\end{aligned}$$

The force constant can be calculated from the expression

$$\tilde{\nu}_e = \frac{1}{2\pi c} \sqrt{\frac{k_f}{\mu}} \quad (\text{Eq. 4.5.17})$$

i.e.

$$k_f = 4\pi^2 c^2 \mu \tilde{\nu}_e^2$$

The reduced mass  $\mu$  for  $^{14}\text{N}^{16}\text{O}$  is

$$\begin{aligned}\mu &= \frac{\{(0.014 \text{ kg})/(6.023 \times 10^{23})\} \{(0.016 \text{ kg})/(6.023 \times 10^{23})\}}{\{(0.014 \text{ kg})/(6.023 \times 10^{23})\} + \{(0.016 \text{ kg})/(6.023 \times 10^{23})\}} \\ &= 1.2397 \times 10^{-26} \text{ kg}\end{aligned}$$

Hence

$$\begin{aligned}k_f &= 4(3.14)^2 (2.998 \times 10^8 \text{ m s}^{-1})^2 (1.2397 \times 10^{-26} \text{ kg}) (1903.98 \times 10^2 \text{ m}^{-1})^2 \\ &= 1.593 \times 10^3 \text{ kg s}^{-2} \approx 1.593 \times 10^3 \text{ N m}^{-1}\end{aligned}$$

The  $v_{\max}$  corresponding to the dissociation energy is given by

$$v_{\max} = \frac{1}{2x_e} - \frac{1}{2} \quad (\text{Eq. 4.5.24})$$

Substituting the value of  $x_e$ , we get

$$v_{\max} = \frac{1}{2 \times 0.007332} - \frac{1}{2} = 67.694 \approx 67.7 \approx 68$$

$$\begin{aligned} \text{Hence } \tilde{E}_D &= \tilde{E}_{\max} = \left( v_{\max} + \frac{1}{2} \right) \tilde{\nu}_e \left\{ 1 - \left( v_{\max} + \frac{1}{2} \right) x_e \right\} \\ &= (68.5) (1903.98 \text{ cm}^{-1}) (1 - 68.5 \times 0.007332) \\ &= 64918.9 \text{ cm}^{-1} = 64918.9 \times 10^2 \text{ m}^{-1} \end{aligned}$$

In the unit of joule, we have

$$\begin{aligned} E_D &= (64918.9 \times 10^2 \text{ m}^{-1}) (6.626 \times 10^{-34} \text{ J s}) (2.998 \times 10^8 \text{ m s}^{-1}) \\ &= 1.29 \times 10^{-18} \text{ J} \end{aligned}$$

The wavenumber corresponding to the true dissociation energy with respect to that of zero-point energy will be given by

$$\tilde{E}_D' = \tilde{E}_D - \tilde{E}_0 = 64918.9 \text{ cm}^{-1} - 948.5 \text{ cm}^{-1} = 63970.4 \text{ cm}^{-1}$$

In the unit of joule, we get

$$\begin{aligned} E_D' &= (63970.4 \times 10^2 \text{ m}^{-1}) (6.626 \times 10^{-34} \text{ J s}) (2.998 \times 10^8 \text{ m s}^{-1}) \\ &= 1.27 \times 10^{-18} \text{ J} \end{aligned}$$

### Example 4.5.3

The vibrational energy levels of CO molecule is given by expression

$$E_v/\text{J mol}^{-1} = 25940 \left( v + \frac{1}{2} \right) - 152 \left( v + \frac{1}{2} \right)^2$$

where  $v$  is the vibrational quantum number. Calculate: (a) The force constant of the molecule. (b) The anharmonicity constant. (c) Zero-point energy. (d) Fundamental vibrational frequency. (e) The energy of the first overtone. (f) The period of vibration and the amplitude of vibration in the lowest vibration level. (g) The number of molecules in the level  $v = 1$  relative to  $v = 0$  level at 500 K. (h) The value of vibrational quantum number which leads to the dissociation of the molecule. (i) The dissociation energy of the CO molecule. Do you expect it to be overestimated?

The energy expression for an anharmonic oscillator is

$$E_v = h\nu_e \left( v + \frac{1}{2} \right) - h\nu_e x_e \left( v + \frac{1}{2} \right)^2$$

The given energy expression per mol is

$$E_v = (25940 \text{ J mol}^{-1}) \left( v + \frac{1}{2} \right) - (152 \text{ J mol}^{-1}) \left( v + \frac{1}{2} \right)^2$$

Hence, the energy per molecule is

$$E_v = (4.307 \times 10^{-20} \text{ J}) \left( v + \frac{1}{2} \right) - (2.524 \times 10^{-22} \text{ J}) \left( v + \frac{1}{2} \right)^2$$

Comparing this with the theoretical expression, we get

$$h\nu_e = 4.307 \times 10^{-20} \text{ J}$$

$$h\nu_e x_e = 2.524 \times 10^{-22} \text{ J}$$

$$\text{Hence } \nu_e = \frac{4.307 \times 10^{-20} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 6.500 \times 10^{13} \text{ s}^{-1}$$

$$x_e = \frac{2.524 \times 10^{-22} \text{ J}}{4.307 \times 10^{-20} \text{ J}} = 5.860 \times 10^{-3}$$

(a) The force constant of the molecule can be calculated from the expression

$$\nu_e = \frac{1}{2\pi} \sqrt{\frac{k_f}{\mu}}$$

Hence  $k_f = (2\pi\nu_e)^2 \mu$

Now  $\mu$  for CO is

$$\begin{aligned} \mu &= \frac{m_C m_O}{m_C + m_O} = \frac{\{(0.012 \text{ kg})/(6.023 \times 10^{23})\} \{(0.016 \text{ kg})/(6.023 \times 10^{23})\}}{\{(0.012 \text{ kg})/(6.023 \times 10^{23})\} + \{(0.016 \text{ kg})/(6.023 \times 10^{23})\}} \\ &= 1.138 \times 10^{-26} \text{ kg} \end{aligned}$$

Thus  $k_f = (2\pi\nu_e)^2 \mu$

$$= \{2(3.14) (6.500 \times 10^{13} \text{ s}^{-1})\}^2 (1.138 \times 10^{-26} \text{ kg})$$

$$= 1.896 \times 10^3 \text{ kg s}^{-2} \approx 1.896 \times 10^3 \text{ N m}^{-1}$$

(b) The anharmonicity constant  $x_e = 5.860 \times 10^{-3}$

(c) For zero-point energy,  $v = 0$ . Hence

$$\begin{aligned} E &= (4.307 \times 10^{-20} \text{ J}) \left( \frac{1}{2} \right) - (2.524 \times 10^{-22} \text{ J}) \left( \frac{1}{2} \right)^2 \\ &= 2.1535 \times 10^{-20} \text{ J} - 0.631 \times 10^{-22} \text{ J} \\ &= 2.1472 \times 10^{-20} \text{ J} \end{aligned}$$

(d) The fundamental vibrational frequency

$$\nu_e = 6.500 \times 10^{13} \text{ s}^{-1}$$

(e) The first overtone corresponds to the transition from  $v = 0$  to  $v = 2$ . The energy difference between these two levels is

$$\begin{aligned} \Delta E &= 2(h\nu_e) (1 - 3x_e) = 2(4.307 \times 10^{-20} \text{ J}) (1 - 3 \times 5.860 \times 10^{-3}) \\ &= 8.463 \times 10^{-20} \text{ J} \end{aligned}$$

(f) The period of vibration is

$$\tau = \frac{1}{\nu} = \frac{1}{6.502 \times 10^{13} \text{ s}^{-1}} = 1.538 \times 10^{-14} \text{ s}$$

Equating zero-point energy with the classical expression of potential energy, we get

$$\begin{aligned} \frac{1}{2} k_f x_{\max}^2 &= 2.1472 \times 10^{-20} \text{ J} \\ x_{\max} &= \left( \frac{2 \times 2.1472 \times 10^{-20} \text{ J}}{k_f} \right)^{1/2} = \left( \frac{2 \times 2.1472 \times 10^{-20} \text{ J}}{1.896 \times 10^3 \text{ N m}^{-1}} \right)^{1/2} \\ &= 4.754 \times 10^{-12} \text{ m} = 4.754 \text{ pm} \end{aligned}$$



(g) We have

$$\frac{N_1}{N_0} = \exp(-\Delta E_1/kT)$$

$$\text{Now } \Delta E_1 = E_1 - E_0 = (h\nu_e)(1 - 2x_e) = (4.307 \times 10^{-20} \text{ J})(1 - 2 \times 0.00586) = 4.256 \times 10^{-20} \text{ J}$$

$$\text{Thus } \frac{N_1}{N_0} = \exp[-(4.256 \times 10^{-20} \text{ J}) / (1.38 \times 10^{-23} \text{ J K}^{-1})(500 \text{ K})] \\ = \exp(-6.168) = 2.95 \times 10^{-3}$$

(h) The quantum number of the vibrational level leading to the dissociation of the molecule is given by

$$v_{\max} = \frac{1}{2x_e} - \frac{1}{2} = \frac{1}{2 \times 0.00586} - \frac{1}{2} = 85.32 - 0.5 = 84.82 \approx 85$$

(i) Substituting  $v_{\max}$  in the given energy expression, we get

$$E/\text{J mol}^{-1} = 25940 \left( v_{\max} + \frac{1}{2} \right) - 152 \left( v_{\max} + \frac{1}{2} \right)^2 \\ = 25940 (85.5) - 152 (85.5)^2 = 1.107 \times 10^6$$

$$\text{Now } E_0/\text{J mol}^{-1} = 25940 \left( \frac{1}{2} \right) - 152 \left( \frac{1}{2} \right)^2 = 12932$$

$$\Delta E_{\text{diss}} = E - E_0 = 1.094 \times 10^6 \text{ J mol}^{-1}$$

The above value of dissociation energy is overestimated as the energy expression does not include higher anharmonicity constants.

The value of  $\tilde{\nu}_e$  is  $4395 \text{ cm}^{-1}$  for  $\text{H}_2$  molecule. Calculate the approximate zero-point energy per mole of  $\text{H}_2$ . If  $\tilde{\nu}_e x_e$  is  $118 \text{ cm}^{-1}$ , what is the exact zero-point energy?

Approximate zero-point energy

$$= \frac{1}{2} h \nu_e = \frac{1}{2} hc \tilde{\nu}_e \\ = \frac{1}{2} (6.626 \times 10^{-34} \text{ J s}) (3 \times 10^8 \text{ m s}^{-1}) (4395 \times 10^2 \text{ m}^{-1}) \\ = 4.368 \times 10^{-20} \text{ J}$$

Hence, approximate zero-point energy per mole

$$= (4.368 \times 10^{-20} \text{ J}) (6.023 \times 10^{23} \text{ mol}^{-1}) \\ = 2.631 \times 10^4 \text{ J mol}^{-1} = 26.31 \text{ kJ mol}^{-1}$$

Exact zero-point energy per mole

$$= \frac{1}{2} N_A hc \tilde{\nu}_e - \frac{1}{4} hc (\tilde{\nu}_e x_e) N_A \\ = 26.31 \times 10^3 \text{ J mol}^{-1} - \frac{1}{4} (6.626 \times 10^{-34} \text{ J s}) (3 \times 10^8 \text{ m s}^{-1}) \\ \times (118 \times 10^2 \text{ m}^{-1}) (6.023 \times 10^{23} \text{ mol}^{-1}) \\ = 25.96 \times 10^3 \text{ J mol}^{-1} = 25.96 \text{ kJ mol}^{-1}$$

### Example 4.5.5

The vibrational potential energy of a diatomic molecule can be represented approximately by the Morse function

$$V = b [1 - \exp\{a(r_{\text{eq}} - r)\}]^2$$

where  $b$  and  $a$  are positive characteristic constants of a molecule,  $r$  is internuclear distance and  $r_{\text{eq}}$  is the equilibrium of  $r$ .

(a) Show that  $V$  has a minimum value at  $r = r_{\text{eq}}$ .

(b) Show that for a small displacement from the equilibrium position, the above function is approximated by a simple harmonic potential. Also show that at  $r = r_{\text{eq}}$

$$(d^2V/dr^2) = k_f$$

(c) Derive the expression of frequency of oscillation,  $\nu$ , in terms of  $b$ ,  $a$  and  $r_{\text{eq}}$ . Also show that  $a = 4.445 \nu \sqrt{\mu/b}$ .

(d) Derive the expression of the dissociation energy in terms of  $b$ ,  $a$  and  $r_{\text{eq}}$ .

(e) For HBr  $b = 6.280 \times 10^{-19} \text{ J}$ ,  $a = 18.11 \text{ nm}^{-1}$  and  $r_{\text{eq}} = 0.1414 \text{ nm}$ , calculate (i)  $k_f$ , (ii)  $\nu$ , (iii) zero-point energy, and (iv) dissociation energy of HBr.

(f) For showing minimum at  $r = r_{\text{eq}}$ , we set  $(dV/dr)r_{\text{eq}} = 0$  and proceed to show that  $(d^2V/dr^2)r_{\text{eq}} > 0$ . Thus, we have

$$\frac{dV}{dr} = 2b[1 - \exp\{a(r_{\text{eq}} - r)\}] [a \exp\{a(r_{\text{eq}} - r)\}] \\ = 2ba \exp\{a(r_{\text{eq}} - r)\} - 2ba \exp\{2a(r_{\text{eq}} - r)\}$$

At  $r = r_{\text{eq}}$ , we have

$$\left( \frac{dV}{dr} \right) = 0$$

$$\text{Now } \frac{d^2V}{dr^2} = -2ba^2 \exp\{a(r_{\text{eq}} - r)\} + 4ba^2 \exp\{2a(r_{\text{eq}} - r)\}$$

At  $r = r_{\text{eq}}$ , we have

$$\frac{d^2V}{dr^2} = 2ba^2 > 0$$

Hence at  $r = r_{\text{eq}}$ ,  $V$  exhibits a minimum value.

(b) For a small displacement, we can write

$$\exp\{a(r_{\text{eq}} - r)\} = 1 + a(r_{\text{eq}} - r) + \dots$$

$$V = b[1 - \{1 + a(r_{\text{eq}} - r) + \dots\}]^2$$

$$= b[-a(r_{\text{eq}} - r) - \dots]^2$$

Retaining only the first term, we have

$$V = ba^2(r_{\text{eq}} - r)^2$$

which is the same as that of the harmonic oscillator (Eq. 4.5.12) provided, we have

$$\frac{1}{2} k_f = ba^2$$

$$\text{or } k_f = 2ba^2$$

$$\text{Since } \left( \frac{d^2V}{dr^2} \right) = 2ba^2$$

(derived in part a)

we have  $k_f = \left( \frac{d^2V}{dr^2} \right)_{r=r_{eq}}$

(c) The frequency of oscillation  $\nu$  is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k_f}{\mu}}$$

Substituting  $k_f = 2ba^2$ , we get

$$\nu = \frac{1}{2\pi} \sqrt{\frac{2ba^2}{\mu}} = \frac{a}{(\sqrt{2})\pi} \sqrt{\frac{b}{\mu}}$$

Rearranging, we get

$$a = (\sqrt{2})\pi\nu \sqrt{\frac{\mu}{b}} = 4.45 \nu \sqrt{\frac{\mu}{b}}$$

(d) The dissociation energy of the molecule is given by

$$D = V(r = \infty) - V(r = r_{eq})$$

From the given expression of Morse function, we have

$$D = b - 0 = b$$

Since the minimum potential energy is not equal to zero but  $(1/2)h\nu$ , we have

$$D = b - \frac{1}{2}h\nu = b - \frac{1}{2} \frac{ha}{2\pi} \sqrt{\frac{2b}{\mu}}$$

(e) We have

$$(i) \quad k_f = 2ba^2$$

$$= 2 (6.280 \times 10^{-9} \text{ J}) (18.11 \times 10^9 \text{ m}^{-1})^2 = 4.119 \times 10^2 \text{ N m}^{-1}$$

$$(ii) \quad \nu = \frac{a}{2\pi} \sqrt{\frac{2b}{\mu}}$$

Now

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\begin{aligned} &= \frac{[(1 \times 10^{-3} \text{ kg}) / (6.023 \times 10^{23})] \{ (79.9 \times 10^{-3} \text{ kg}) / (6.023 \times 10^{23}) \}}{\{ (1 \times 10^{-3} \text{ kg}) / (6.023 \times 10^{23}) \} + \{ (79.9 \times 10^{-3} \text{ kg}) / (6.023 \times 10^{23}) \}} \\ &= \frac{79.9 \times 10^{-3}}{80.9 \times 6.023 \times 10^{23}} \text{ kg} = 1.64 \times 10^{-27} \text{ kg} \end{aligned}$$

$$\text{Thus } \nu = \left( \frac{18.11 \times 10^9 \text{ m}^{-1}}{2 \times 3.14} \right) \left( \frac{2 \times 6.28 \times 10^{-19} \text{ J}}{1.64 \times 10^{-27} \text{ kg}} \right)^{1/2} = 7.98 \times 10^{13} \text{ s}^{-1}$$

(iii) Zero-point energy

$$\begin{aligned} &= \frac{1}{2} h\nu = \frac{1}{2} (6.626 \times 10^{-34} \text{ J s}) (7.98 \times 10^{13} \text{ s}^{-1}) \\ &= 2.64 \times 10^{-20} \text{ J} \end{aligned}$$

### Example 4.5.6

#### Solution

$$(iv) \quad D = b - \frac{1}{2}h\nu = 6.280 \times 10^{-19} \text{ J} - 2.64 \times 10^{-20} \text{ J} = 6.02 \times 10^{-19} \text{ J}$$

The wavenumber corresponding to the equilibrium vibrational frequency of iodine molecule is  $215 \text{ cm}^{-1}$ , and the anharmonicity constant is 0.003. At 300 K, what is the intensity of the hot band relative to that of the fundamental absorption?

For calculating the relative intensities of transitions, we first of all calculate the relative populations in  $v = 0, 1$  and 2 vibrational levels. The energies of these levels are as follows.

$$v = 0: \quad \tilde{E}_0 = \frac{1}{2} \tilde{\nu}_e \left( 1 - \frac{1}{2} x_e \right) = 107.339 \text{ cm}^{-1}$$

$$v = 1: \quad \tilde{E}_1 = \frac{3}{2} \tilde{\nu}_e \left( 1 - \frac{3}{2} x_e \right) = 321.094 \text{ cm}^{-1}$$

$$v = 2: \quad \tilde{E}_2 = \frac{5}{2} \tilde{\nu}_e \left( 1 - \frac{5}{2} x_e \right) = 533.469 \text{ cm}^{-1}$$

$$\begin{aligned} \text{Now } \Delta \tilde{E}_{v=1 \leftarrow v=0} &= \Delta \tilde{E}_1 = 321.049 \text{ cm}^{-1} - 107.339 \text{ cm}^{-1} = 213.71 \text{ cm}^{-1} \\ &= 213.71 \times 10^3 \text{ m}^{-1} \end{aligned}$$

$$\Delta E_1 = \Delta \tilde{E}_1 hc$$

$$\begin{aligned} &= (213.71 \times 10^3 \text{ m}^{-1}) (6.626 \times 10^{-34} \text{ J s}) (2.998 \times 10^8 \text{ m s}^{-1}) \\ &= 4.245.295 \times 10^{-24} \text{ J} \end{aligned}$$

$$\frac{N_1}{N_0} = \exp(-\Delta E_1/kT)$$

$$\begin{aligned} &= \exp[-(4.245.295 \times 10^{-24} \text{ J}) / (1.38 \times 10^{-23} \text{ J K}^{-1}) (300 \text{ K})] \\ &= \exp(-1.0254) = 0.3581 \end{aligned}$$

$$\begin{aligned} \Delta \tilde{E}_{v=2 \leftarrow v=0} &= \Delta \tilde{E}_2 = 533.469 \text{ cm}^{-1} - 107.339 \text{ cm}^{-1} = 426.13 \text{ cm}^{-1} \\ &= 426.13 \times 10^3 \text{ m}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta E_2 &= (426.13 \times 10^3 \text{ m}^{-1}) (6.626 \times 10^{-34} \text{ J s}) (2.998 \times 10^8 \text{ m s}^{-1}) \\ &= 8.464.965 \times 10^{-24} \text{ J} \end{aligned}$$

$$\frac{N_2}{N_0} = \exp(-\Delta E_2/kT)$$

$$\begin{aligned} &= \exp[-(8.464.965 \times 10^{-24} \text{ J}) / (1.38 \times 10^{-23} \text{ J K}^{-1}) (300 \text{ K})] \\ &= \exp(-2.0446) = 0.1295 \end{aligned}$$

If the intensity of transition is assumed to be proportional to the number of molecules in the state from which the transition occurs, then the intensity of hot band will be about 0.36 of that of the fundamental transition. If we assume it to be proportional to the difference in populations of involved levels, then the ratio of intensities would be given by

$$\frac{\text{Difference of population in } v=1 \text{ and } v=2 \text{ levels}}{\text{Difference of population in } v=0 \text{ and } v=1 \text{ levels}}$$

$$= \frac{(0.3581 - 0.1295)}{(1.0 - 0.3581)} = \frac{0.2286}{0.6419}$$

$$= 0.356 \approx 0.36$$

#### 4.6 VIBRATION-ROTATION SPECTRA OF DIATOMIC MOLECULES

Under the Born-Oppenheimer approximation, the molecule may be considered to execute rotation and vibration motions quite independently of each other. This follows from the fact that the vibrational energy is much larger than the rotational energy. The total energy of a molecule executing both vibration and rotation motions may be taken as the sum of the separate energies, i.e.

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} \quad (4.6.1)$$

Thus, the energies of molecules belonging to the same vibrational level may differ depending upon their rotational energies.

The energy of a molecule executing both vibrational and rotational motions may be represented as shown in Fig. 4.6.1.

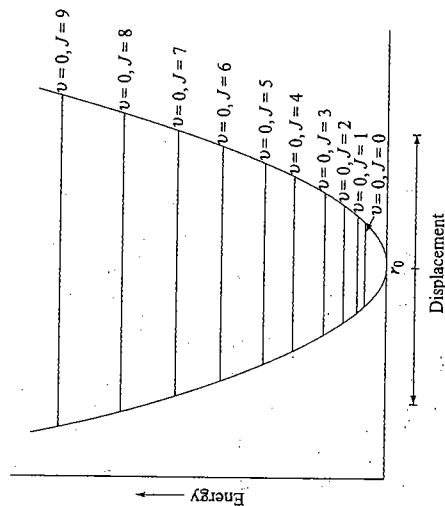


Fig. 4.6.1 Different rotational levels associated with the lowest vibrational level

The lines shown in Fig. 4.6.1 represent the different rotational levels in the lowest vibrational level, i.e.  $v=0$ . Similarly the energies of rotational levels associated with the excited vibrational state can be displayed (Fig. 4.1.1). The energy may be presented by the symbol  $E_{v,J}$ , where the first and second subscripts represent the vibrational and rotational quantum numbers, respectively. For example,  $E_{0,1}$  and  $E_{1,0}$  represent the energies in the zero vibrational level and first rotational level, and first vibrational level and zero rotational level, respectively.

At room temperature, most of molecules are associated with the lowest vibrational level and with many of the associated rotational levels. In fact, the

distribution of molecules in the rotational levels associated with the lowest vibrational level is the same as that of pure rotational levels as shown in Fig. 4.4.3.

If we consider a molecule to execute anharmonic oscillations and rigid rotations, its energy in the wavenumber unit will be given by the expression

$$\tilde{E}_{\text{total}} = BJ(J+1) + \left(v + \frac{1}{2}\right) \tilde{\nu}_e \left\{1 - x_e \left(v + \frac{1}{2}\right)\right\} \quad (4.6.2)$$

where the various symbols have their usual meanings.

A molecule on absorbing the radiation corresponding to the vibrational excitation may simultaneously be accompanied by the change in the rotational level. The spectrum exhibiting such transitions is known as vibration-rotation spectrum. It can be shown that the selection rules for such transitions are the same as those for each separately. Thus, we have

$$\Delta v = \pm 1, \pm 2, \text{ etc.}$$

$$\Delta J = \pm 1$$

Since  $\Delta J$  equal to zero is not allowed, it follows that a vibrational change will always be accompanied by a simultaneous rotational change.

Let  $v'', J''$  and  $v', J'$  be the vibrational and rotational quantum numbers of the lower and upper energy levels, respectively. The difference between these two levels in the unit of wavenumber will be

$$\tilde{\Delta E} = [BJ'(J'+1) - BJ''(J''+1)]$$

$$+ \left[ \left(v' + \frac{1}{2}\right) \tilde{\nu}_e \left\{1 - x_e \left(v' + \frac{1}{2}\right)\right\} - \left(v'' + \frac{1}{2}\right) \tilde{\nu}_e \left\{1 - x_e \left(v'' + \frac{1}{2}\right)\right\} \right] \quad (4.6.4)$$

If we restrict to  $v' = 1 \leftarrow v'' = 0$  transition, we will have

$$\tilde{\Delta E} = B(J' - J'') (J' + J'' + 1) + \tilde{\nu}_e (1 - 2x_e) \quad (4.6.5)$$

Since  $\Delta J = \pm 1$ , we will have

Transitions with  $\Delta J = +1$ , i.e.  
 $J' = J'' + 1$

$$\text{Hence } \tilde{\Delta E} = 2B(J'' + 1) + \tilde{\nu}_e (1 - 2x_e) \quad (4.6.6)$$

where  $J''$  can have values 0, 1, 2, ..., and so on.

Transitions with  $\Delta J = -1$ , i.e.

$$J' = J'' - 1 \quad \text{or} \quad J'' = J' + 1$$

$$\text{Hence } \tilde{\Delta E} = -2B(J' + 1) + \tilde{\nu}_e (1 - 2x_e) \quad (4.6.7)$$

where  $J'$  can have the values 0, 1, 2, ..., and so on.

Equations (4.6.6) and (4.6.7) may be combined into one expression as

$$\Delta \tilde{E} = 2Bm + \tilde{\nu}_e(1 - 2x_e) \quad (4.6.8)$$

where  $m$  can have values  $\pm 1, \pm 2, \dots$ , and so on. The symbol  $m$  represents  $(J'' + 1)$  in case of  $\Delta J = +1$  and  $(J' + 1)$  in case of  $\Delta J = -1$ . Positive and negative values of  $m$  correspond to  $\Delta J = +1$ , and  $\Delta J = -1$ , respectively.

### Vibration-Rotation Spectrum

Equation (4.6.8) describes the combined vibration-rotation spectrum. Since  $m$  can have values  $\pm 1, \pm 2, \dots$ , it follows that the spectrum will consist of equally spaced lines (spacing  $2B$ ) on each side of the wave number  $\tilde{\nu}_e(1 - 2x_e)$  as shown in Fig. 4.6.2.

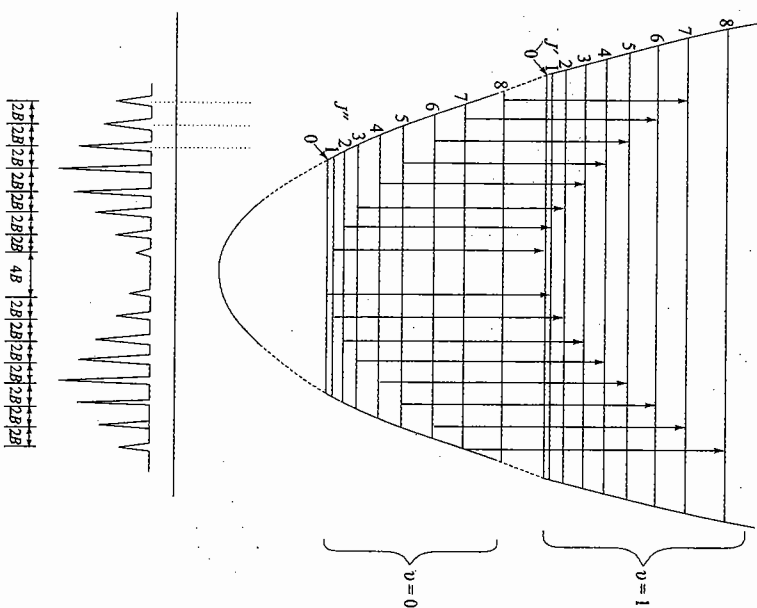


Fig. 4.6.2 A typical vibration-rotation spectrum

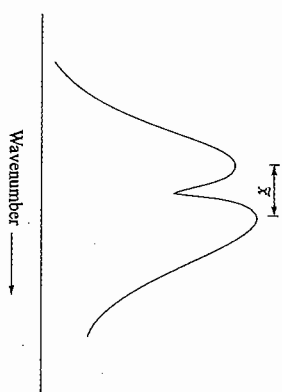
The absorption line corresponding to  $\tilde{\nu}_e(1 - 2x_e)$  will not appear as  $m$  cannot be equal to zero. This wavenumber is referred to as band centre or *band origin* or *Q branch* of the spectrum. The lines to the low wavenumber side of band centre correspond to the negative values of  $m$  and represent transitions corresponding to the negative value of  $\Delta J$ , i.e. these transitions correspond to  $J' = 0 \leftarrow J'' = 1$ ,  $J' = 1 \leftarrow J'' = 2$ , and so on. These lines are referred to as *P branch* of the spectrum. The lines corresponding to the high wavenumber side of band centre correspond

Fig. 4.6.3 Vibration-rotation spectrum under very low resolution

### Application of Vibration-Rotation Spectrum

to the positive values of  $m$  and hence represent transitions corresponding to the positive values of  $\Delta J$ , i.e. these transitions correspond to  $J' = 1 \leftarrow J'' = 0$ ,  $J' = 2 \leftarrow J'' = 1$ , and so on. These lines are referred to *R branch* of the spectrum. (The labelling as P, Q, and R branches can be extended if in addition to  $\Delta J = \pm 1$ , the values 0 and  $\pm 2$  are also allowed. The labelling of branches goes as follows. lines arising from  $\Delta J = -2$  -1 0 +1 +2 labelling of the branch O P Q R S.)

The intensities of lines in P and R branches will be of the type exhibited by the pure rotation spectrum. The spectrum shown in Fig. 4.6.2 will be observed only by the high resolving spectrometer. If the resolving power is not high, one will observe the spectrum as shown in Fig. 4.6.3.



The vibration-rotation spectrum can be utilized to determine all those molecular parameters which can be determined separately from the pure vibration and pure rotation spectra. The location of band centre corresponding to the transition  $v' = 1 \leftarrow v'' = 0$  (the fundamental transition) and  $v' = 2 \leftarrow v'' = 0$  (the first overtone) helps in providing the values  $\tilde{\nu}_e$  and  $x_e$ , and hence the value of force constant. The separation of lines in either P branch or R branch provides the value of  $2B$  and hence the values of moment of inertia and the bond length.

The approximate value of parameter  $B$  can even be evaluated if the rotational lines are not resolved, i.e. from the spectrum shown in Fig. 4.6.3.

The quantum number of the rotational level having maximum population is given by

$$J = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} \quad (\text{Eq. 4.4.12})$$

This quantum level will produce the maximum intensity of the rotational transition. Now since  $m = \pm (J + 1)$ , we have

$$m_{\max} = \pm \left( \sqrt{\frac{kT}{2Bhc}} + \frac{1}{2} \right)$$

and hence the maxima of P and R branches will be located at

$$\tilde{\Delta E} = \pm 2B \left( \sqrt{\frac{kT}{2Bhc}} + \frac{1}{2} \right) + \tilde{\nu}_e (1 - 2x_e) \quad (\text{Eq. 4.6.8})$$

and hence the separation between them is

$$\tilde{\Delta E} = 4B \left( \sqrt{\frac{kT}{2Bhc}} + \frac{1}{2} \right) = \sqrt{\frac{8kTB}{hc}} + 2B$$

The factor  $2B$  is much smaller than the factor  $\sqrt{8kTB/hc}$  and hence the above relationship can be approximated to

$$\tilde{\Delta E} \approx \sqrt{\frac{8kTB}{hc}}$$

$$\text{or } B \approx \frac{hc x_e^2}{8kT} \quad (4.6.9)$$

### Problem 4.6.1

(a) Show that the expression of wavenumber for the transitions  $\nu' = 1 \leftarrow \nu'' = 0$  and  $\Delta J = \pm 2$  (i.e. O and S branches of vibrational-rotational spectrum) is given by

$$\tilde{\Delta E} = \pm 2Bm + \tilde{\nu}_e (1 - 2x_e)$$

where  $m = 2J'' + 3$  for  $\Delta J = +2$  transitions and  $m = 2J' + 3$  for  $\Delta J = -2$  transitions.

(b) Show that the separation between the maxima of O and S branches is given by

$$\Delta \tilde{\nu} = \sqrt{\frac{32BkT}{hc}} + 8B$$

(c) Calculate the rotational constants for  $\text{HgCl}_2$  at 555 K if the separation between the maxima of O and S branches is  $23.8 \text{ cm}^{-1}$ .

(a) From Eq. (4.6.5), we have

$$\tilde{\Delta E} (\nu' = 1 \leftarrow \nu'' = 0; J' \leftarrow J'') = B(J' - J'') (J' + J'' + 1) + \tilde{\nu}_e (1 - 2x_e)$$

For O branch ( $\Delta J = -2$ ), we have

$$J' = J'' - 2 \quad \text{or} \quad J'' = J' + 2; \quad J' = 0, 1, 2, \dots$$

$$\text{Hence } \tilde{\Delta E} = -2B(2J' + 3) + \tilde{\nu}_e (1 - 2x_e) \quad (1)$$

For S branch ( $\Delta J = +2$ ), we have

$$J' = J'' + 2; \quad J'' = 0, 1, 2, \dots$$

$$\text{Hence } \tilde{\Delta E} = 2B(2J'' + 3) + \tilde{\nu}_e (1 - 2x_e) \quad (2)$$

Writing Eqs (1) and (2) together, we have

$$\tilde{\Delta E} = \pm 2Bm + \tilde{\nu}_e (1 - 2x_e) \quad (3)$$

where  $m = 2J' + 3$  and can have values 3, 5, 7, ...

$$\text{(b) Now } J_{\text{max}} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} \quad (\text{Eq. 4.4.12})$$

$$\text{Hence } m_{\text{max}} = 2 \sqrt{\frac{kT}{2Bhc}} + 2$$

Thus,  $\tilde{\Delta E}$  at  $m = m_{\text{max}}$  is given by

$$\tilde{\Delta E} = \pm 2B \left( 2 \sqrt{\frac{kT}{2Bhc}} + 2 \right) + \tilde{\nu}_e (1 - 2x_e)$$

The separation between the maxima of O and S branches is given by

$$\Delta \tilde{\nu} = 4B \left( 2 \sqrt{\frac{kT}{2Bhc}} + 2 \right) = \sqrt{\frac{32BkT}{hc}} + 8B$$

(c) Since  $8B$  is smaller than  $\sqrt{32BkT/hc}$ , we may write

$$\Delta \tilde{\nu} = \sqrt{\frac{32BkT}{hc}} \quad \text{or} \quad B = \left( \frac{hc}{32kT} \right) (\Delta \tilde{\nu})^2$$

Substituting the values, we get

$$B = \frac{(6.626 \times 10^{-34} \text{ J s})(3 \times 10^{10} \text{ cm s}^{-1})^2}{(32)(1.38 \times 10^{-23} \text{ J K}^{-1})(555 \text{ K})} (23.8 \text{ cm}^{-1})^2$$

$$= 0.04595 \text{ cm}^{-1}$$

## 4.7 VIBRATION SPECTRA OF POLYATOMIC MOLECULES

### Number of Fundamental Vibrations

A system consisting of  $N$  particles can be described by specifying three coordinates for each particle, i.e. a total of  $3N$  coordinates. Even when these particles are undergoing motions, however complicated they may be, the system at any instant can be described by stating these  $3N$  coordinates. Since any one of these components can vary by any amount, the system is said to possess  $3N$  independent components of motion or degrees of freedom. If  $N$  particles are bound to form a molecule, then the  $3N$  degrees of freedom are conveniently chosen as follows.

**Translational Motion** The translational motion of a molecule as a whole can be described by the motion of its centre of mass. Since three coordinates are required to describe the position of centre of mass, three degrees of freedom are required in describing the translational motion of the molecule.

**Rotational Motion** A linear molecule can rotate about two mutually perpendicular axes whereas a nonlinear molecule can rotate about three axes. Thus, two degrees of freedom are utilized in describing the rotational motion of a linear molecule and three for those of a nonlinear molecule.

**Vibrational Motion** The remaining  $(3N - 5)$  degrees of freedom for a linear molecule and  $(3N - 6)$  for a nonlinear molecule are utilized in describing the internal vibrations (stretching and bending motions) of the molecule. In other words, a linear molecule has  $(3N - 5)$  fundamental vibrations (or normal modes of vibration) whereas a nonlinear molecule has  $(3N - 6)$  fundamental vibrations. Since a molecule consisting of  $N$  atoms contains a total of  $(N - 1)$  bonds between its atoms,  $(N - 1)$  vibrations out of  $(3N - 5)$  or  $(3N - 6)$  modes of vibrations are those of bond stretching motions and the remaining  $(2N - 4)$  or  $(2N - 5)$  are those of bending motions. The former motions involve the change in bond lengths whereas the latter involve the change in bond angles of the molecule.

Table 4.7.1 describes the normal modes of vibrations of di-, tri- and tetra-atomic molecules.

Table 4.7.1 Normal Modes of Vibrations of Di-, Tri- and Tetra-Atomic Molecules

Molecule	Number of atoms $N$	Total degrees of freedom	Number of modes of vibrations	Number of motions of	
				Bond stretching ( $N-1$ ) or ( $3N-6$ )	Bending ( $2N-4$ ) or ( $2N-5$ )
Diatomic; $H_2, O_2, HCl$ , etc.	2	6	1	1	0
			Symmetric stretching $\leftarrow H-H \rightarrow$		
Nonlinear triatomic; $SO_2, H_2O$ , etc.	3	9	3	2	1
			Symmetric stretching 	Symmetric bending 	
			Antisymmetric stretching 		
Linear triatomic; $CO_2, N_2O$ , etc.	3	9	4	2	2
			Symmetric stretching <sup>1</sup> 	Symmetric bending (doubly degenerate) <sup>3</sup> 	
			Antisymmetric stretching <sup>2</sup> 		
			Symmetric bending (doubly degenerate) <sup>3</sup> 		
Linear tetra-atomic;	4	12	7	3	4
Acetylene			Symmetric stretching 	Antisymmetric stretching 	Bending (doubly degenerate) 

- Two outer atoms move in opposite directions, the central one is stationary.
- Two outer atoms move in one direction, the central one in opposite direction.
- The outer atoms move in opposite directions approximately at right angles to the molecular axis and the valence angle at the central atom changes.

### Infrared Spectrum of a Polyatomic Molecule

A polyatomic molecule exhibits  $(3N-5)$  or  $(3N-6)$  normal modes of vibrations. These vibrations fall into two categories, viz., *skeletal vibration* and *group vibrations*. The former involves more or less all atoms of the molecule and in the latter vibrations of a small group of atoms are more vigorous than those of the remaining atoms.

Skeletal vibrations exhibit absorptions below  $1500\text{ cm}^{-1}$  which are characteristics of the molecule as a whole. These may be utilized to establish the general structure of the molecule such as the linear structure, branched structure, benzenoid structure and so on.

Since the bands observed in the region below  $1500\text{ cm}^{-1}$  are characteristic of the compound in question, this region is known as the *fingerprint region*. The use of the fingerprint region to confirm the identity of the molecule with an authentic sample is considered to be one of the most reliable methods.

Group vibrations involve the vibrations of the various functional groups or other characteristic groups present in the molecule. Such vibrations are usually independent of the structure of the molecule as a whole and exhibit absorptions in the region above  $1500\text{ cm}^{-1}$ . A few functional groups exhibit the absorption in the fingerprint region.

Some commonly encountered group absorption wavenumbers are listed in Table 4.7.2.

Table 4.7.2 Characteristic Group Absorption Wavenumbers

Bond	Group	Description	Approximate wavenumber $\text{cm}^{-1}$
C—H	$CH_3$ , alkane	stretching	2 960, 2 870
C—H	$CH_2$ , alkane	stretching	2 920, 2 850
C—H	$-CH=CH-$	stretching	3 095–3 010
C—H	$\equiv C-H$	stretching	3 300
C—H	$-C-H$ , aromatic	stretching	3 100–3 030
C—H	$-CH_2-$	bending	1 470–1 400
C—H	$-C-CH_3$	bending	1 380–1 360
C—H	$-CH=CH-$ , trans	bending	1 300, 970
C—H	$-CH=CH-$ , cis	bending	690
C—C	$(CH_2)_3C-$	skeletal	1 250
C—C	$-(CH_2)_n$ ( $n > 3$ )	skeletal	725
C—C	$-CH=CH-$	stretching	1 680–1 620
C—C	$-C\equiv C-$	stretching	2 230
C—H	$C_6H_5-$ (monosubstituted aromatic)	CH wag	1 600, 1 500
O—C	$\text{>C=O}$	stretching	1 760–1 690
O—C	$\text{>C-O-}$	stretching	1 250–1 000
C—N	$\text{>C=N-}$	stretching	1 690–1 630
O—H	O—H (free)	stretching	3 620
O—H	O—H	stretching	3 600–3 300
N—H	(hydrogen bonded, alcohols)	stretching	3 500–3 000
S—H	$N-H_x$ ( $x = 1, 2, 3$ )	stretching	2 600
Cl—C	Cl—C	stretching	800–700

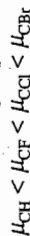
The group frequencies follow approximately the equation

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k_f}{\mu}} \quad (\text{Eq. 4.5.17a})$$

Thus for one type of group, the group frequency increases with increase in force constant of the bond and decreases with increase in the reduced mass of the group. For example, in the group  $\text{—C—X}$ , where X may be H, F, Cl, Br, the group frequencies follow the relation



since the reduced mass of the group follows the order



The triple bond shows absorption at higher frequency than double bonds and double bonds higher than single bonds, since the bond strength or the force constant follows the relation



In general, the infrared spectrum of a polyatomic molecule may be complex owing to the appearance of overtones, and combination and difference bands corresponding to  $\nu_1 + \nu_2$  and  $\nu_1 - \nu_2$ , respectively, where  $\nu_1$  and  $\nu_2$  are the frequencies of the two fundamental modes of vibrations. Besides this, the two close frequencies of vibrations undergo changes due to the mutual interactions. For example, one of the fundamental transition of  $\text{CO}_2$  is at  $1330 \text{ cm}^{-1}$  and one of the overtone transition is at  $1334 \text{ cm}^{-1}$ . This close by transitions are referred to as accidental degeneracy. Due to mutual interactions, these are shifted to  $1285 \text{ cm}^{-1}$  and  $1388 \text{ cm}^{-1}$ , respectively. Also the intensity of the overtone transition is very much enhanced at the expense of the fundamental transition. This type of shifting of intensities is known as *Fermi resonance*. Nevertheless, the infrared spectrum is very helpful in detecting the functional groups and the general structure of the molecule. Moreover, shifts of observed group frequencies can often be used to infer the nature of the bonding of adjacent groups in the molecule.

## 4.8 RAMAN SPECTRA

### Introduction

Let a beam of monochromatic light from the visible portion of the spectrum be chosen such that it is not absorbed by the substance under study. If such a light is passed through the substance, nearly all of it is transmitted and a very small fraction of it is scattered in all directions (Fig. 4.8.1). If the scattered light in a direction perpendicular to the incident beam is spectrographed, it is found not only to contain a line corresponding to the frequency of incident light, but also a pattern of relatively weak lines on the low-frequency side of the incident light and a similar pattern of still more weak lines on the high-frequency side (Fig. 4.8.2).

Fig. 4.8.1 Scattering of light by nonabsorbing substance

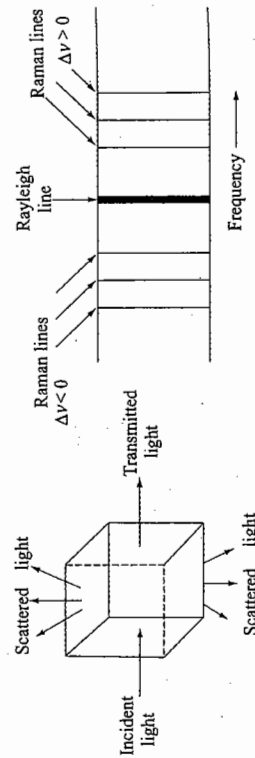
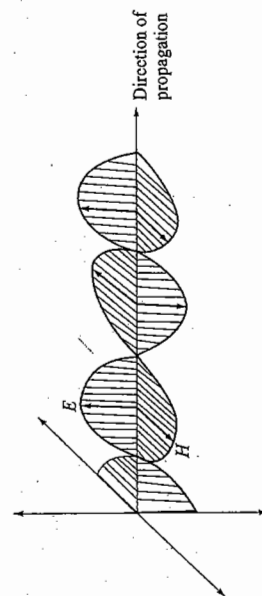


Fig. 4.8.2 Schematic representation of a Raman spectrum

Fig. 4.8.3 The variation of electric component of the radiation with time



† See Section 3.2

The line at the incident frequency is known as *Rayleigh line* (after Lord Rayleigh who carried out a lot of study in the field of light scattering). The other weak lines are called the *Raman lines* (after C.V. Raman who was the discoverer of these lines). The difference between the frequencies (or wavenumbers) of the Rayleigh line and a Raman line is known as the *Raman shift*, and may be expressed as

$$\Delta\nu = |\nu_0 - \nu_k| \quad (4.8.1a)$$

$$\Delta\tilde{\nu} = |\tilde{\nu}_0 - \tilde{\nu}_k| \quad (4.8.1b)$$

where the subscripts 0 and R stand for incident and Raman lines, respectively.

For a given substance, the Raman shift is found to be independent of the frequency of the incident radiation, i.e. it has the same value for different frequency of the incident light. The difference is a characteristic of the substance and is found to be equal to its vibrational or rotational transition.

The Raman spectroscopy is observed only when there occurs a periodic change in the polarizability of molecule due to its vibrational or rotational oscillation. From the classical point of view the above fact may be understood as follows.

In the presence of a static electric field, a molecule is polarized, i.e. the positively charged nuclei and the negatively charged electronic cloud is attracted towards the respective oppositely charged pole of the electric field. Consequently, the molecule acquires an induced dipole moment which is given by†

$$p_{\text{ind}} = \alpha E \quad (4.8.2)$$

where  $\alpha$  is the polarizability of the molecule.

In the presence of a beam of radiation, the molecule also acquires an induced dipole moment due to the electrical component of the incident light. This electrical component is not static but varies as the sine (or cosine) wave according to the equation

$$E = E_0 \sin(2\pi\nu t) \quad (4.8.3)$$

where  $\nu$  is the frequency of radiation and  $t$  is the time. This variation is illustrated in Fig. 4.8.3. Consequently, the induced dipole moment also oscillates according to the equation

$$p = \alpha E = \alpha E_0 \sin(2\pi\nu t) \quad (4.8.4)$$



According to the electromagnetic theory, an oscillating dipole emits radiation of its own frequency. This explains the occurrence of Rayleigh line in the light scattered by the substance. The presence of Raman lines is due to the periodic change in the value of  $\alpha$  due to the internal vibrational or rotational motion† according to the equation

$$\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial \xi} \right) \xi_0 \sin(2\pi \nu_f) \quad (4.8.5)$$

where  $\partial \alpha / \partial \xi$  is the change in polarizability with the displacement coordinate  $\xi$ ,  $\nu_f$  the frequency of internal motion, and  $\alpha_0$  is the polarizability in the equilibrium position  $\xi_0$ .

The periodic change in the polarizability will also change periodically the induced dipole moment (Eq. 4.8.2). When this periodic change is superimposed upon the periodic oscillation due to the electrical component of light (Eq. 4.8.4), we get

$$\begin{aligned} p_{\text{ind}} &= \left\{ \alpha_0 + \left( \frac{\partial \alpha}{\partial \xi} \right) \xi_0 \sin 2\pi \nu_f \right\} E_0 \sin 2\pi \nu \\ &= \alpha_0 E_0 \sin(2\pi \nu) + \left( \frac{\partial \alpha}{\partial \xi} \right) \xi_0 E_0 \sin(2\pi \nu_f) \sin(2\pi \nu) \end{aligned} \quad (4.8.6)$$

Since  $2 \sin \theta \sin \phi = \cos(\theta - \phi) - \cos(\theta + \phi)$ , we get

$$\begin{aligned} p_{\text{ind}} &= \alpha_0 E_0 \sin(2\pi \nu) + \frac{1}{2} \left( \frac{\partial \alpha}{\partial \xi} \right) \xi_0 E_0 \cos\{2\pi(\nu - \nu_f)t\} \\ &\quad - \frac{1}{2} \left( \frac{\partial \alpha}{\partial \xi} \right) \xi_0 E_0 \cos\{2\pi(\nu + \nu_f)t\} \end{aligned} \quad (4.8.7)$$

that is, induced dipole moment of the molecule not only oscillates with frequency  $\nu$ , but also with frequencies  $\nu - \nu_f$  and  $\nu + \nu_f$ . It is thus expected that besides the frequency  $\nu$ , the oscillating dipole will also emit radiations of frequencies  $\nu - \nu_f$  and  $\nu + \nu_f$ . These radiations appear as the Raman lines in the light scattered by the substance.

Note that if  $\partial \alpha / \partial \xi$  is zero, i.e. there occurs no change in the polarizability during the small displacement from the equilibrium position of the internal motion, then the induced dipole moment of the molecule will oscillate with only one frequency corresponding to the frequency of incident light. In such a case, the molecule emits only Rayleigh line and hence Raman lines are not observed, i.e. the molecule is Raman inactive. Thus, the essential criterion for a molecule to be Raman active is that a molecular vibration or rotation must cause a change in the component of molecular polarizability. This criterion may be compared with those of rotational

† The dipole moment induced in a molecule by an electric field besides depending on the internuclear distance also depends on the orientation of the molecule with respect to the field. Thus, a change in polarizability is also expected during the molecular rotation.

## Quantum Explanation of Raman Lines

and vibrational spectroscopy which respectively are: (1) the molecule must have a permanent dipole moment, and (2) there should occur a change in dipole moment during the vibration motion.

Since the polarizability has the dimension of volume in gaussian units (see, Section 3.3) it may be concluded that only those vibrations which are associated with the change in the volume will be Raman active.

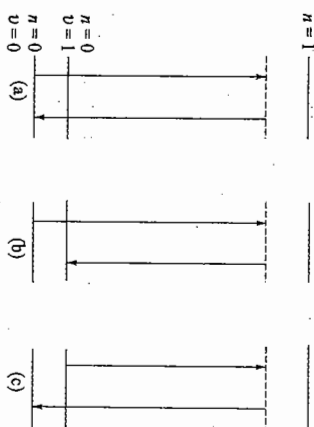
The Raman lines are, in general, of very weak intensities as compared to the Rayleigh line. From the qualitative quantum viewpoint, the occurrence of Raman lines may be understood as follows.

The photon on colliding with a molecule will constitute either an elastic or inelastic collision. We may consider the molecule to form a complex with the photon during the extremely short time of collision ( $\approx 10^{-15}$  s). The energy of the complex will not correspond to a molecular electronic energy level (Fig. 4.8.4a). Now if the collision is elastic, the complex will dissociate to give the molecule and photon of the same energy which it had before the collision. This gives rise to the Rayleigh scattering. On the other hand, if the collision is inelastic, there can occur an exchange of energy between molecule and photon. This exchange of energy can be of two types.

- The molecule before the collision occupies a lower vibrational or rotational energy level and after the emission of the photon, it may be present in any one of the higher energy levels as permitted by the selection rule. In this case, the molecule gains energy equivalent to the energy difference between the two involved levels. This energy is provided by the photon and hence its energy is decreased and thus a Raman line on the low frequency side is observed (Fig. 4.8.4b).
- The molecule before the collision occupies one of the higher vibrational or rotational energy level and after the emission of the photon may be present in any one of the lower energy levels as permitted by the selection rule. In this case, the molecule loses an energy equivalent to the energy difference between the two involved levels. This energy is gained by the photon and hence its energy is increased and thus a Raman line on the high frequency side is observed (Fig. 4.8.4c).

Fig. 4.8.4 Schematic representation of

- (a) Rayleigh scattering with  $\Delta v = 0$ ,  
(b) Raman scattering with  $\Delta v < 0$ , and  
(c) Raman scattering with  $\Delta v > 0$





### Pure Rotational Raman Spectra of Diatomic Molecules

The selection rules for the pure rotational Raman spectra of diatomic molecules are  $\Delta J = 0$  and  $\pm 2$ .

The selection rule  $\Delta J = 0$  gives rise to the Rayleigh scattering only. The selection rule  $\Delta J = \pm 2$  gives rise to the Raman lines. The factor 2 is due to the fact that the polarizability ellipsoid rotates twice as fast as the rotation of the molecule.<sup>†</sup>

The rotational energy expression is  $\tilde{E}_J = BJ(J+1)$  (Eq. 4.4.7)

The difference in wavenumber between two levels is

$$\Delta \tilde{E} = BJ'(J' + 1) - BJ''(J'' + 1) \quad (\text{Eq. 4.4.14})$$

For the selection rule  $\Delta J = J' - J'' = 2$ , we have

$$\begin{aligned} \Delta \tilde{E} &= B(J'' + 2)(J'' + 3) - BJ''(J'' + 1) \\ &= B(4J'' + 6); \quad J'' = 0, 1, 2, \dots \end{aligned} \quad (4.8.8)$$

Similarly for the selection rule  $\Delta J = J' - J'' = -2$ , we have

$$\begin{aligned} \Delta \tilde{E} &= -B(4J' + 6); \quad J' = 0, 1, 2, \dots \\ \text{Thus, Raman lines will appear at wave numbers given by the expression} \\ \tilde{\nu} &= \tilde{\nu}_0 \pm B(4J + 6); \quad J = 0, 1, 2, 3, \dots \end{aligned} \quad (4.8.9)$$

where  $\tilde{\nu}_0$  is the wavenumber of Rayleigh line. The lines at wavenumbers less than  $\tilde{\nu}_0$  are known as *Stokes' lines* and those having wavenumbers greater than  $\tilde{\nu}_0$  are known as *anti-Stokes' lines*. The expected pure rotational Raman spectrum is shown in Fig. 4.8.5.

The first Stokes' and anti-Stokes' lines will lie at a separation of  $6B$  from the Rayleigh line. The remaining lines will lie at a constant spacing of  $4B$ .

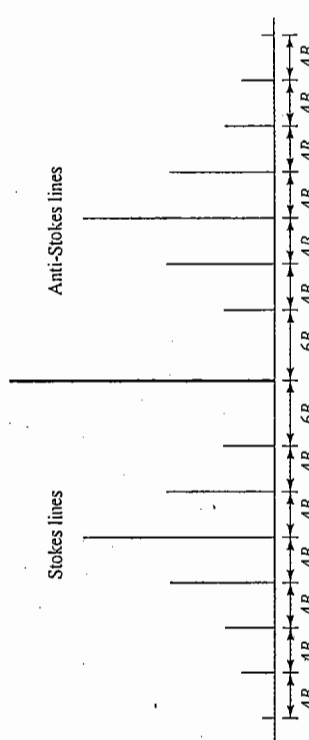


Fig. 4.8.5 An expected pure rotational Raman spectrum for a diatomic molecule

### Intensities of Pure Rotational Raman Spectra

The intensities of Raman lines will, as usual, depend on the population of the initial level where from the molecules are promoted or demoted to the final level. For Stokes' lines,  $J_{\text{initial}} < J_{\text{final}}$ , whereas for anti-Stokes' lines  $J_{\text{initial}} > J_{\text{final}}$  (Fig. 4.8.5). Since the population in the rotational levels is as shown in Fig. 4.4.3, it is expected that the intensities of Stokes' and anti-Stokes' lines also have the same appearance.

For molecules having a centre of symmetry, the nuclear spins also affect the population in the rotational levels. For molecules having nuclear spin zero (e.g.  $\text{O}_2$

and  $\text{CO}_2$ ), every alternative rotational level is unoccupied. For example, the levels  $J'' = 0, 2, 4, \dots$  in case of  $\text{O}_2$  and  $J'' = 1, 3, 5, \dots$  in case of  $\text{CO}_2$  are unoccupied. Consequently, the first Stokes and anti-Stokes absorptions in Raman rotational spectrum of  $\text{O}_2$  occur at  $\tilde{\nu}_0 - 10B$  and  $\tilde{\nu}_0 + 10B$ , respectively, and those of  $\text{CO}_2$  occur at  $\tilde{\nu}_0 - 6B$  and  $\tilde{\nu}_0 + 6B$ , respectively, with the remaining absorptions in both cases occur at the interval of  $8B$ . For molecules having nonzero nuclear spin (e.g.  $\text{H}_2$  and  $\text{N}_2$ ), the rotational levels show alternation in population as given by the following expression.<sup>†</sup>

*Half-integral spin* even  $J :: I(2I+1) : (I+1)(2I+1) :: I : (I+1)$

*Integral spin* even  $J :: (I+1)(2I+1) : I(2I+1) :: (I+1) : I$

where  $I$  is the nuclear spin quantum number. There facts are reflected in the Raman rotational spectra. For  $\text{H}_2(I = 1/2)$ , the alternation in intensities is  $1 : 3$  while for  $\text{N}_2(I = 1)$ , it is  $2 : 1$ .

The pure rotational Raman spectra provides the value  $B$ . Thus, the moment of inertia and bond length of the molecule can be determined. The usefulness of Raman spectroscopy may be emphasized here. Homonuclear diatomic molecules do not exhibit pure vibrational or rotational spectra as they possess no dipole moment. But they do exhibit rotational Raman spectra and hence structural parameters which cannot be determined by pure rotational spectra can be determined from the Raman spectra.

The selection rules for the vibrational Raman spectra are the same as those for pure vibrational spectra, i.e.

$$\Delta v = \pm 1, \pm 2, \dots$$

For a vibrational mode, the vibrational energy expression is

$$\tilde{E}_v = (v + 1/2) \tilde{\nu}_e \{1 - (v + 1/2)x_e\} \quad (\text{Eq. 4.5.20})$$

The differences in energy levels are

$$v' = 1 \leftarrow v'' = 0; \quad \Delta \tilde{E}_{\text{fundamental}} = \tilde{\nu}_e (1 - 2x_e)$$

$$v' = 2 \leftarrow v'' = 0; \quad \Delta \tilde{E}_{\text{overtone}} = 2 \tilde{\nu}_e (1 - 3x_e)$$

$$v' = 2 \leftarrow v'' = 1; \quad \Delta \tilde{E}_{\text{hot}} = \tilde{\nu}_e (1 - 4x_e)$$

Since the population in  $v = 1, v = 2$ , etc., levels are very small, the overtones and hot lines are of very weak intensities as compared to the fundamental line. Restricting only to the fundamental transition, we will observe Raman lines at the following wave numbers:

$$\tilde{\nu}_{\text{fundamental}} = \tilde{\nu}_0 \pm \tilde{\nu}_e (1 - 2x_e)$$

where the minus sign represents the Stokes' line and the plus sign refers to the anti-Stokes' line. Since the latter refers to the transitions  $v' = 0 \leftarrow v'' = 1$ , it is expected to be very weak as very few molecules exit in the  $v'' = 1$  state at normal temperature. On increasing temperature, the population of  $v = 0$  state is decreased whereas that of  $v = 1$  state is increased. It is, thus, expected that the intensity of Stokes' line will

<sup>†</sup> The given expressions represent the ratio of nuclear wave functions associated with the corresponding rotational levels. See, Annexure II of the Chapter 4 of Volume 5.

<sup>†</sup> Since the polarizability  $\alpha$  is an even function, the transition moment integral  $P_{mm} = \langle \psi_m | \hat{\alpha} | \psi_n \rangle$  will be nonzero if the product of  $\psi_m$  and  $\psi_n$  is an even function, i.e. both  $\psi_m$  and  $\psi_n$  are either even or odd functions. This leads to the selection rule  $\Delta J = \pm 2$ .

decrease whereas that of anti-Stokes line will increase on increasing the temperature of the sample.

As mentioned earlier, only those vibrational modes will be Raman active for which  $\partial\alpha/\partial\xi$  is nonzero. A molecule with little or no symmetry, all of its vibrational modes are usually Raman active. But a molecule with a considerable symmetry, it is not so. Moreover, the symmetric vibrations produce a large value of  $\partial\alpha/\partial\xi$  near the equilibrium position of vibration and hence produce intense Raman lines. For antisymmetric vibrations,  $\partial\alpha/\partial\xi$  is either zero or usually very small and hence they produce either no line or weak (and sometimes unobservable) Raman lines.

In general, the rotational fine structure associated with the vibrational Raman spectrum of a large molecule is ignored as it is beyond resolution. Only in case of diatomic gaseous molecules, the resolution is sufficient to be analyzed with the rigid-rotator model. Thus, we write

$$\tilde{E}_{v,J} = Bv(J+1) + (v+1/2)\tilde{\nu}_e \{1 + (v+1/2)x_e\}$$

The selection rules are

$$\Delta v = \pm 1, \pm 2, \dots \quad \text{and} \quad \Delta J = 0, \pm 2$$

Restricting to the fundamental vibration transition, we have

$$\Delta J = 0; \quad \Delta\tilde{E}_Q = \tilde{\nu}_e(1 - 2x_e); \quad (\text{for all } J)$$

$$\Delta J = +2; \quad \Delta\tilde{E}_S = \tilde{\nu}_e(1 - 2x_e) + B(4J'' + 6); \quad (J'' = 0, 1, 2, \dots)$$

$$\Delta J = -2; \quad \Delta\tilde{E}_O = \tilde{\nu}_e(1 - 2x_e) - B(4J' + 6); \quad (J' = 0, 1, 2, \dots)$$

where the subscripts Q, S and O refer to the Q, S and O branches, respectively. If  $\tilde{E}_0$  is the wavenumber of the exciting radiation, Stokes' lines will be observed at the following wavenumbers.

$$\tilde{E}_Q = \tilde{E}_0 - \Delta\tilde{E}_Q; \quad \tilde{E}_S = \tilde{E}_0 - \Delta\tilde{E}_S; \quad \tilde{E}_O = \tilde{E}_0 - \Delta\tilde{E}_O$$

Much weaker anti-Stokes' lines will occur at the same distance from  $\tilde{E}_0$  towards the high wavenumber side.

### Example 4.8.1

For acetone a normal mode of vibration that involves the stretching of the carbonyl bond is active in both Raman and infrared spectra. The Raman line associated with this normal mode is found at 547 nm when excited by incident light whose wavelength is 500 nm. Calculate the wavelength of the centre of the corresponding infrared absorption band.

Frequency of the Raman line at wavelength 547 nm is

$$\nu_1 = \frac{c}{\lambda} = \frac{c}{547 \times 10^{-9} \text{ m}}$$

Frequency of the incident light of wavelength 500 nm is

$$\nu_2 = \frac{c}{\lambda} = \frac{c}{500 \times 10^{-9} \text{ m}}$$

Change in frequency of the light is

$$\Delta\nu = \frac{c}{500 \times 10^{-9} \text{ m}} - \frac{c}{547 \times 10^{-9} \text{ m}} = \frac{c(47 \times 10^{-9} \text{ m})}{(500 \times 10^{-9} \text{ m})(547 \times 10^{-9} \text{ m})}$$

The change in frequency of the light is related to the energy difference between the two vibrational levels. Hence, the wavelength of the centre of the corresponding infrared absorption band is

$$\lambda = \frac{c}{\Delta\nu} = \frac{(500 \times 10^{-9} \text{ m})(547 \times 10^{-9} \text{ m})}{(47 \times 10^{-9} \text{ m})} = \left(\frac{500 \times 547}{47}\right) \times 10^{-9} \text{ m} = 5.819 \times 10^{-6} \text{ m} = 5.819 \text{ }\mu\text{m}$$

A general rule, known as the rule of mutual exclusion, for molecules having centre of symmetry has been established. This rule states that:

*If a molecule has a centre of symmetry, then Raman active vibrational modes are infrared inactive, and vice versa.*

Thus by comparing Raman and infrared spectra of a substance, it is possible to establish whether the molecule has a centre of symmetry or not and hence its structure can be established. If the two spectra do not include the common absorptions, it implies that the molecule has a centre of symmetry. On the other hand, if the two spectra include common lines, it implies that the molecule has no centre of symmetry.

The rule of mutual exclusion may be exemplified by taking the examples of  $\text{CO}_2$  and  $\text{SO}_2$  molecules. The structure of  $\text{CO}_2$  is linear and thus it possesses the centre of symmetry. The molecule of  $\text{SO}_2$  is nonlinear and thus it does not possess the centre of symmetry. The  $\text{CO}_2$  molecule has four vibrational modes, whereas the  $\text{SO}_2$  molecule has three vibrational modes. These modes along with the associated change in the dipole moment and polarizability are described in the following.

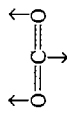
#### 1. Symmetrical Stretch $\leftarrow \text{O}=\text{C}=\text{O} \rightarrow$

During this vibration, the dipole moment of the molecule remains zero throughout the vibration, i.e. the dipole moment does not alter periodically, and hence this vibrational mode will be *infrared inactive*. Since during the vibration, volume of the molecule changes, it may be concluded that there occurs a change in the polarizability of the molecule and hence this vibrational mode will be *Raman active*. More precisely, the slope of the  $\alpha$  versus  $\xi$  curve will be nonzero near the equilibrium position of the vibrational motion, i.e. the small displacement near the equilibrium position produces a change in the polarizability.

#### 2. Antisymmetric Stretch $\text{O}=\text{C}=\text{O}$

Since during the vibration, one of the bond undergoes stretching whereas the other bond undergoes shortening of the bond length it is expected that there will occur a change in dipole moment of the molecule and hence this vibrational mode will be *infrared active*. Since the lengthening and shortening of bonds occur by the same amounts, it is expected that the polarizability (or volume) of the molecule does not change during the vibration. More precisely,  $d\alpha/d\xi = 0$  near the equilibrium position of the vibrational motion. Thus, this vibrational mode will be *Raman inactive*.

### 3. Bending Mode (doubly degenerate)



During the bending motion, the dipole moment of the molecule changes but not its polarizability and hence this vibrational mode will be *infrared active* and *Raman inactive*.

Thus, we see that if a vibrational mode of  $\text{CO}_2$  is infrared active, it is necessarily Raman inactive, on the other hand, if it is infrared inactive, then it is Raman active. This is due to the fact that the  $\text{CO}_2$  molecule has a centre of symmetry.

Coming to the  $\text{SO}_2$  molecule, we will find that all the three vibrational modes are infrared and Raman active. The analysis of symmetric stretch is described below.

The sulphur dioxide molecule has a permanent dipole moment and its value changes periodically during the symmetrical stretch vibrational mode. Since the volume of the molecule changes during the vibration, it is expected that there will also occur a change in polarizability of the molecule. Hence, this vibrational mode will be infrared as well as Raman active.

### Application of Infrared and Raman Spectra

Infrared and Raman spectra supplement each other in the determination of molecular structure. Both types of spectra are needed to determine the structure of the molecule. One of the rules which helps establishing the centre of symmetry in the molecule has been described above. Besides this rule, the following rules are also helpful.

- If the molecule is linear, then all those vibrational modes in which linearity of the molecule is preserved will exhibit only PR contours in the vibration-rotation spectrum. The vibrational modes in which linearity is destroyed will include PQR contours. Thus, if one or more bands in the infrared spectrum contains only PR contour we can conclude that the molecule is linear.
- In general, a symmetric vibration gives rise to a polarized or partially polarized Raman line (a light which has its electrical vector confined to a particular plane) while an antisymmetric vibration gives a depolarized line. In general, the degree of depolarization of the Raman line for a particular type of vibration decreases with increasing molecular symmetry.

- In most cases the absorption lines follow the order:

$$\begin{aligned} \nu_{\text{bending}} &< \nu_{\text{stretch}} \\ \nu_{\text{sym stretch}} &< \nu_{\text{antisym stretch}} \end{aligned}$$

The first condition is due to the fact that the bond-length deformation is more difficult (and hence requires more energy) than the bond-angle deformation.

With these additional rules, one can often assign the structure of simple molecules and also the nature of fundamental modes of vibration associated with the observed infrared or Raman lines. The following problems illustrate the use of above rules in establishing the structure of simple molecules.

### Problem 4.8.1

For  $\text{CO}_2$ , the following spectroscopic data are available. Predict the geometry of  $\text{CO}_2$  molecule.

Wavenumber cm <sup>-1</sup>	Infrared	Raman
1 330	Inactive	Active
2 349	Active (I) (PR)	Inactive
667.3	Active (L) (PQR)	Inactive

The analysis of data is given below.

1. Since transition at 2 349 cm<sup>-1</sup> includes PR contour, we may conclude that the molecule  $\text{CO}_2$  is linear.

2. The infrared and Raman spectra do not include any common line and hence the molecule of  $\text{CO}_2$  contains the centre of symmetry.

Hence, the structure of  $\text{CO}_2$  is  $\text{O}=\text{C}=\text{O}$ .

The  $\text{CO}_2$  molecule exhibits 4 (= 3 × 3 - 5) fundamental vibration modes. These are symmetric stretch, antisymmetric stretch and doubly degenerate bending vibration. Since during symmetric stretch vibration, the dipole moment of  $\text{CO}_2$  does not change whereas its polarizability does change, the transition at 1,330 cm<sup>-1</sup> may be assigned to the symmetric stretch. The transition at 2 349 cm<sup>-1</sup> which include only PR contour may be assigned to antisymmetric stretch, since during this mode the linearity of the molecule is not changed. Lastly, the transition at 667.3 cm<sup>-1</sup> may be assigned to the bending vibrational mode. This assignment also follows from the fact that (i) the transition includes PQR contour (linearity is lost during vibration), and (ii) bending vibration is easy to carry out than the stretching as in the latter, changes in the bond length occur whereas in the former only bond angle is changed. The above assignment is also shown in Table 4.8.1. The assignment is also supported by the information on parallel and perpendicular vibrations shown in the given data.

Table 4.8.1 Assignment of Vibrational Modes

Wavenumber cm <sup>-1</sup>	Assignment
1 330	Symmetric stretch $\leftarrow \text{O}=\text{C}=\text{O} \rightarrow$
2 349	Antisymmetric stretch (parallel vibration) $\text{O}=\text{C}=\text{O}$ $\rightarrow \leftarrow$
667.3	Bending (perpendicular vibration) $\text{O}=\text{C}=\text{O}$ $\updownarrow$

**Problem 4.8.2**

For  $\text{N}_2\text{O}$ , the following spectroscopic data are available. predict the geometry of  $\text{N}_2\text{O}$  molecule.

Wavenumber $\text{cm}^{-1}$	Infrared	Raman
589	Active (PQR)	Inactive
1 285	Active (PR)	Active (polarized)
2 224	Active (PR)	Active (depolarized)

**Solution**

The analysis of data is given below.

1. Since the transition at  $1\,285\text{ cm}^{-1}$  includes PR contour, we may conclude that the molecule of  $\text{N}_2\text{O}$  is linear.
  2. The infrared and Raman spectra contain some common lines. Thus, we may conclude the absence of centre of symmetry in the  $\text{N}_2\text{O}$  molecule. Hence, the structure of  $\text{N}_2\text{O}$  is  $\text{N}\equiv\text{N}=\text{O}$
- The assignment of modes of vibration along with the reasons is given in Table 4.8.2.

**Table 4.8.2 Assignment of Vibrational Modes**

Wavenumber $\text{cm}^{-1}$	Assignment	Reasons
1 285	Symmetric stretch $\text{N}\rightarrow\text{N}-\text{O}\rightarrow$	Linearity of the molecule is maintained (PR contour in infrared spectrum). Raman line is polarized.
2 224	Antisymmetric stretch $\text{N}-\text{N}-\text{O}\rightarrow$ $\rightarrow\text{N}-\text{N}-\text{O}$	Linearity of the molecule is maintained (PR contour in infrared spectrum). Raman line is depolarized.
589	Bending $\text{N}-\text{N}-\text{O}$ $\downarrow\quad\quad\downarrow$	Linearity of the molecule is lost (PQR contour in infrared spectrum). Minimum energy is required for bond bending.

**Problem 4.8.3**

For  $\text{SO}_2$ , the following spectroscopic data are available. Predict the geometry of  $\text{SO}_2$  molecule.

Wavenumber $\text{cm}^{-1}$	Infrared	Raman
519	Active (II) (PQR)	Active (polarized)
1 151	Active (II) (PQR)	Active (polarized)
1 361	Active (L) (PQR)	Active (depolarized)

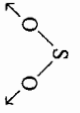


**Solution**

The analysis of the data is given below.

1. Since all transitions include PQR contour, it may be concluded that the molecule is nonlinear.
2. The infrared and Raman spectra involve common lines and hence the absence of centre of symmetry is concluded. This also follows from the fact that a nonlinear triatomic molecule cannot have a centre of symmetry.
3. Since some Raman lines are polarized, it indicates that the symmetry of the molecule is preserved during the vibration. This gives an indication that the two oxygen atoms are placed symmetrically with respect to sulphur atom.

Hence, the structure of  $\text{SO}_2$  is  $\text{O}=\text{S}=\text{O}$ . The assignment of modes of vibration along with the reasons is given in Table 4.8.3. The assignment is also supported by the information on parallel and perpendicular vibrations shown in the given data.

**Table 4.8.3 Assignment of Vibrational Modes**

Wavenumber $\text{cm}^{-1}$	Assignment	Reasons
1 151	Symmetric stretch 	Raman line is polarized. (Parallel vibration)
1 361	Antisymmetric stretch 	Raman line is depolarized. (Perpendicular vibration)
519	Bending 	Raman line is polarized. Minimum energy for bond deformation. (Parallel vibration)

**Problem 4.8.4**

For acetylene, the following spectroscopic data are available. Deduce its structure.

Wavenumber $\text{cm}^{-1}$	Infrared	Raman
3 374	Inactive	Active (polarized)
1 974	Inactive	Active (polarized)
3 287	Active (PR)	Inactive
612	Inactive	Active (weak)
729	Active (PQR)	Inactive

The analysis of the given data is given below.

1. Since the line at  $3\,287\text{ cm}^{-1}$  includes PR contour, it may be concluded that the molecule is linear.

2. Since infrared and Raman spectra do not contain any common line, the presence of centre of symmetry may be concluded.

Hence, the structure of acetylene is  $\text{H}-\text{C}\equiv\text{C}-\text{H}$ .

The assignment of modes of vibration along with the reasons is given in Table 4.8.4.

Table 4.8.4 Assignment of Vibrational Modes

Wavenumber $\text{cm}^{-1}$	Assignment	Reasons
3 374	Symmetric stretch $\text{H}-\text{C}\equiv\text{C}-\text{H}$ $\leftarrow \text{C} \rightarrow \text{C} \rightarrow$	No change in dipole moment during the vibration (infrared inactive), polarizability changes during the vibration (Raman active). Raman line is polarized.
1 974	Symmetric stretch $\text{H}-\text{C}\equiv\text{C}-\text{H}$ $\leftarrow \text{C} \leftarrow \text{C} \rightarrow$	No change in dipole moment during the vibration (infrared inactive). Polarizability changes during the vibration (Raman active). Raman line is polarized.
3 287	Antisymmetric stretch $\text{H}-\text{C}\equiv\text{C}-\text{H}$ $\leftarrow \text{C} \rightarrow \text{C} \leftarrow$	Dipole moment changes during the vibration (infrared active). No change in polarizability during the vibration (Raman inactive). Linearity of the molecule is maintained (PR contour).
612 doubly degenerate	Bending $\uparrow \text{H}-\text{C}\equiv\text{C}-\text{H}$ $\downarrow$	No change in the dipole moment during the vibration (infrared inactive.)
729 degenerate doubly	Bending $\uparrow \text{H}-\text{C}\equiv\text{C}-\text{H}$ $\downarrow$	Change in dipole moment during the vibration. Linearity of the molecule is lost during the vibration (infrared active)

## 4.9 ELECTRONIC SPECTRA OF DIATOMIC MOLECULES

### Introduction

The electron in a diatomic molecule can be excited from an occupied molecular orbital to an empty or partially filled higher molecular orbital. This constitutes what is known as *electronic transition*. The radiation required for the electronic transition lies in the visible or ultraviolet region. A molecule in each stable electronic level can execute vibrational and rotational motions. Following the Born-Oppenheimer approximation, we can write the total energy of the molecule as

$$E_{\text{total}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} \quad (4.9.1)$$

The various vibrational and rotational levels associated with each stable electronic level have been shown schematically in Fig. 4.1.1.

The electronic transitions are accompanied by changes in vibrational and rotational energy levels. The vibrational transitions appear as the *coarse structure* whereas as rotational transitions as the *fine structure*.

For a transition of the vibrational coarse structure of spectra, we may write

$$\Delta E = \Delta E_{\text{elec}} + \Delta E_{\text{vib}} \quad (4.9.2)$$

### Franck-Condon Principle

For a given electronic transition, there is no quantum mechanical restriction (i.e. the selection rules) on the change in the vibrational quantum number. Since in the ground electronic-state most molecules occupy the lowest vibrational level, all types of transitions from this lowest vibrational level to any of vibrational levels of the higher electronic state are possible. Experimentally, it is known that all such transitions are not equally intense. This fact can be explained with the help of *Franck-Condon principle*, which may be stated as follows.

*The electronic transition occurs so quickly that the internuclear separation during the transition remains unchanged.*

Thus, the instantaneous internuclear separation in the excited electronic state is the same as it was in the initial ground state at the time of electronic transition. Since the internuclear separation remains the same, the transition in the energy diagram will be shown by a *vertical line* as shown in Fig. 4.9.1. The probability or intensity of transition at a particular internuclear separation depends on the probabilities of finding the molecule in the two involved vibrational levels at the given internuclear separation. A transition involving the largest probabilities in the lower and excited vibrational levels will be the most intense. Other transitions will have lesser probabilities and thus will have lesser intensities. Figure 4.9.1 illustrates a few electronic transitions in accordance with the Franck-Condon principle. Transition labelled as b in Fig. 4.9.1 will be more intense than the other two shown transitions.

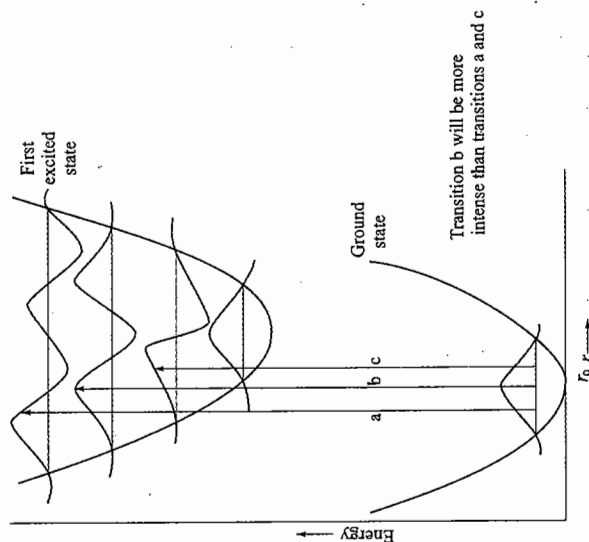


Fig. 4.9.1 A schematic illustration of Franck-Condon principle

The exact nature of electronic spectrum depends on the internuclear separation of the molecule in the excited state relative to that in the ground state. In general, the internuclear separation in the excited state is slightly larger and the force constant is slightly smaller than those in the ground state. This follows from the fact that the excited state usually corresponds to a weak bond in the molecule. Consequently, the depth in the potential energy diagram of the excited state is slightly displaced towards the larger internuclear distance and the spacing between the associated vibrational levels is smaller than those of the lower electronic state.

Figure 4.9.2 displays typical electronic spectra when there occurs (a) no change, (b) a little change, and (c) a larger change in internuclear distance of the excited state relative to the ground state. In 4.9.2c continuum indicates that all radiations are absorbed causing the molecule to dissociate. The energy excess of dissociation limit is utilized in imparting kinetic energies to the dissociated atoms.

### Dissociation of Molecule

If the internuclear separation in the excited state is much larger than in the lower level, the electronic transition may lead to the dissociation of the molecule (Fig. 4.9.2c). This happens when the vertical transition ends at a point where the

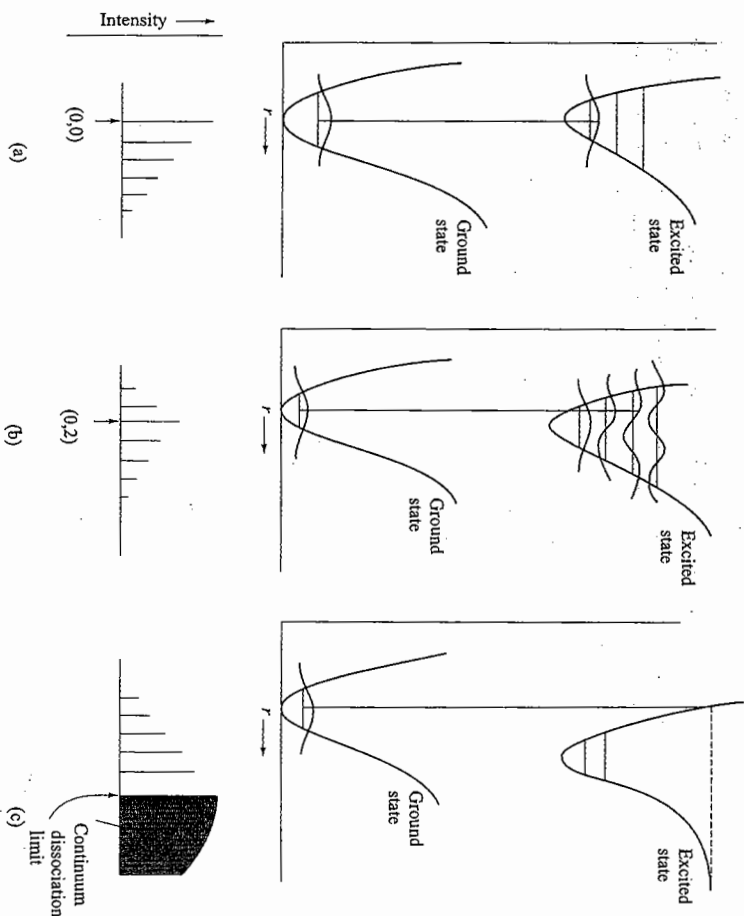
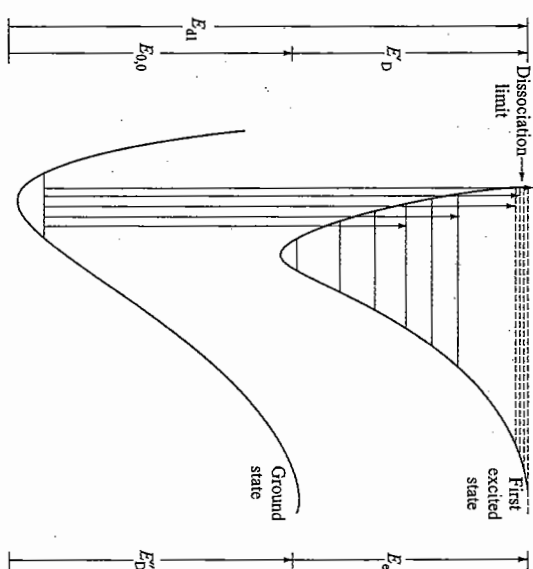


Fig. 4.9.2 Typical electronic spectra, (a) with no change, (b) a little change, and (c) a larger change in internuclear separation in the excited state relative to the ground state

Fig. 4.9.3 A schematic representation of dissociation on excitation



where  $E_D$  is the dissociation energy of the molecule in the ground electronic state and  $E_{ex}$  is the excitation energy of one of the atoms produced on dissociation (Fig. 4.9.3). From Fig. 4.9.3, we can also write

$$E_{0,0} + E_D = E_D + E_{ex} \quad (4.9.4)$$

$$E_D = E_D + E_{ex} - E_{0,0} \quad (4.9.5)^{\dagger}$$

$$E_{0,0} = E_D + E_{ex} \quad (4.9.6)$$

where  $E_{0,0}$  and  $E_{ex}$  represent the energy of dissociation limit and the extra energy, respectively. In most cases, only one of the dissociation atoms produced as a result of absorption of energy  $E_{0,0}$  is in its electronic excited state and the other one is in its ground electronic state. Thus, the energy  $E_{0,0}$  may be written as

$$E_{0,0} = E_D + E_{ex} \quad (4.9.7)$$

electronic energy of the molecule in the excited state is larger than the corresponding dissociation energy. In the present case, electronic spectrum generally consists of the coarse structure (corresponding to the different changes in vibrational quantum number) which ends at a continuum representing the *dissociation limit* of the spectrum. This continuum is observed because of the fact that the kinetic energy with which products of dissociation (which is equal to the excess energy in the final state above that needed just for the dissociation of the molecule) is not quantized. Thus, in the continuum region, we may write

<sup>†</sup> The value of  $E_D$  can also be determined with the help of Birge and Sponer extrapolation method where  $\Delta E$  involving the neighbouring vibrational absorptions (e.g.,  $\Delta E(v' = 1 \leftarrow v'' = 0) - \Delta E(v' = 2 \leftarrow v'' = 0)$  is plotted against the vibrational quantum number  $v'$ . A smooth curve passing through these points is drawn and is extrapolated up to the  $v' = 0$  axis. Since the dissociation energy of the molecule is equivalent to the sum of all  $\Delta E$  plotted above, the area under the curve of  $\Delta E$  versus  $v'$  directly gives the required dissociation energy of the molecule in the excited state.



Alternatively, the molecule (e.g.  $H_2$  molecule) is dissociated if the electron is excited to the unstable electronic state (no minimum energy in the energy curve). This is shown in Fig. 4.9.4. The electronic spectrum in this case consists of only continuum.

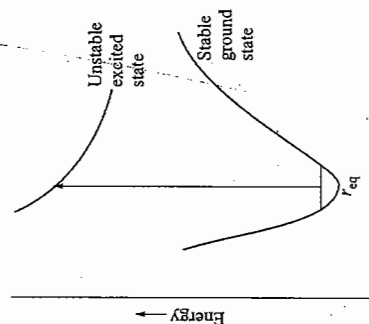


Fig. 4.9.4 Dissociation of the molecule on excitation to the unstable excited state

#### Predissociation of Molecule

In some cases, the coarse (vibrational) and fine (rotational) structures of electronic spectrum are quite distinct for small and large changes in the vibrational quantum number, but in the central region a continuum is observed. This behaviour, which is known as predissociation, can be explained by the energy diagram shown in Fig. 4.9.5. This diagram is observed when for a particular geometry near to the end of the molecular vibration, the energy of the molecule in the stable electronic excited state is identical with that in the unstable electronic excited state, vis-à-vis, the two

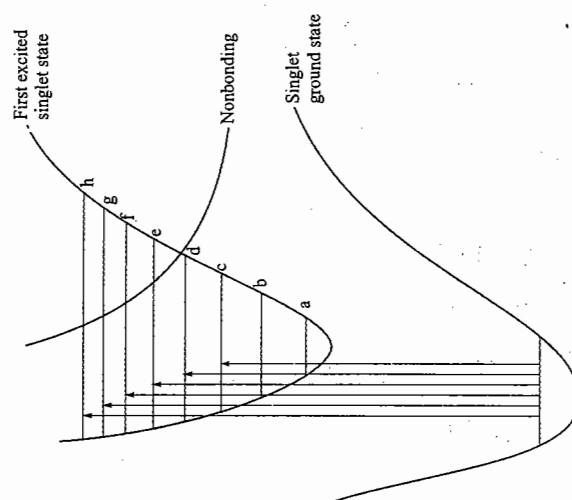


Fig. 4.9.5 A schematic illustration of predissociation

energy curves intersect each other at this geometry. There is high probability (since the molecule spends larger time near the extreme ends of vibrational motion for larger value of vibrational quantum number) that the molecule during vibration may shift over from the stable to unstable configuration of this geometry. For distance smaller and larger than this geometry, the probability of crossing over decreases rapidly as the probability of finding the molecule at other distances is small.

Now if the electronic excitation ends with the low and high vibrational quantum levels in the excited state (e.g. levels  $a$ ,  $b$ ,  $g$  and  $h$  in Fig. 4.9.5), it is expected to exhibit normal coarse and fine structures, but if it ends at the vibrational level where inter-crossing occurs, the molecule can cross over from stable to unstable electronic state when the molecule is at the extreme of vibration leading to the dissociation of the molecule and hence a continuum.

Normally, fine structure is not resolvable unless the resolution is sufficiently good. The resolution of fine structure is possible only for some substances present in the gaseous phase. In the liquid or dissolved states, the perturbing effect of neighbouring molecules smears out all or nearly all of the fine structure observed in the gas phase. This fine structure can be rationalized under the Born-Oppenheimer approximation and with the help of the energy expressions for the various energy levels of a diatomic molecule.

Finally, a few application of electronic spectra of diatomic molecules may be described. The electronic spectrum is often helpful in establishing the electronic structure of a molecule. It can also provide data on the dissociation energy of the molecule. Homonuclear molecules (e.g.  $H_2$ ,  $N_2$ ) separately do not exhibit pure rotational (as they do not have permanent dipole moment) and pure vibrational (as component of dipole moment does not change during vibration) spectra, but because of the necessary change in dipole moment during electronic transition, they do exhibit coarse and fine structures. From these structures the relevant information about the molecule may be obtained.

A few lines about the electronic transitions in polyatomic molecules may be added here. At the outset it may be stated that the spectrum is usually very complex and in few cases, correlation between the absorption band and the type of transition is possible. But a broad classification of the type of electronic transition and the range in which it occurs may be made. These are:

- (i)  $\sigma \rightarrow \sigma^*$  transition  $\lambda$  lies in ultraviolet or far ultraviolet region as  $\sigma$  electrons are held more firmly in the molecule.
- (ii)  $\pi \rightarrow \pi^*$  transition  $\lambda$  lies in the near ultraviolet region and visible regions.
- (iii)  $n \rightarrow \pi^*$  transition  $\lambda$  lies in the visible region of light. Normally they have very weak intensities as their excitation involves different region of the molecule.

**Fluorescence**

A photon which is absorbed by the molecule may be emitted as such and can be displayed in the emission spectrum. In this case, absorption and emission spectra are identical. In many cases, these two spectra are not identical especially when the excitation ends at a higher vibrational level. Generally, the emission spectrum is slightly shifted to the longer wavelength (red shift). This fact has been attributed to the *radiationless decay* (or *thermal degradation*) of the energy. What happens that the excess vibrational energy is transferred to the neighbouring molecules during the intermolecular collisions. This transference appears as the kinetic energy and hence heating effects are produced. When the excited molecule reaches the lowest vibrational level of the excited electronic state, the electron comes back to the ground electronic state and hence emits radiation which is of higher wavelength (low frequency) than that of the absorbed photon. The above mechanism is identified as the *fluorescence* and the emission spectrum is called the *fluorescent spectrum* (Fig. 4.9.6). The time between initial absorption and emission is of the order of  $10^{-8}$  s.

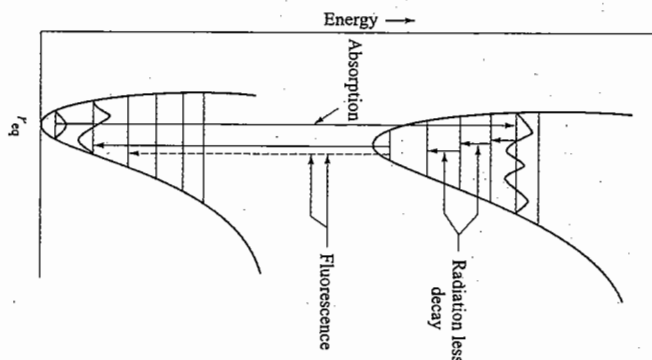


Fig. 4.9.6 Schematic representation of fluorescence

**Phosphorescence**

In some cases, the emission of radiation is delayed (may be by seconds, minutes or more) and this results into what is known as *phosphorescence*. This phenomenon has been explained by the energy diagram shown in Fig. 4.9.7. This diagram is observed when for a fixed geometry, the energy of the molecule in the two stable electronic excited states (singlet and triplet) is identical, vis-à-vis, the two energy curves intersect each other at this point. There is some probability that the molecule undergoes *intersystem crossing* where during the vibration it shifts over from the singlet to triplet state.

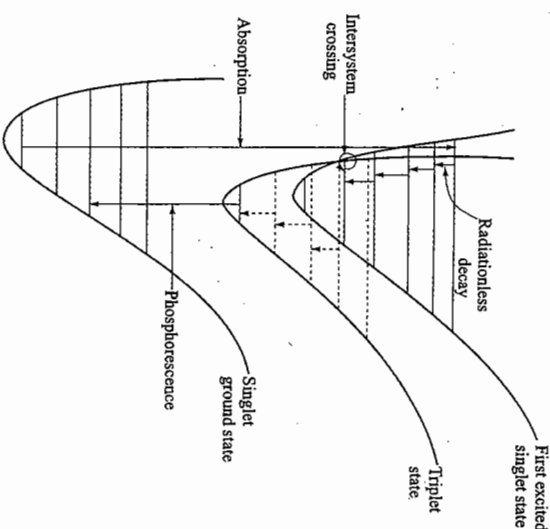


Fig. 4.9.7 Schematic representation of phosphorescence

**Explanation of Singlet and Triplet States**

Before describing the mechanism of phosphorescence, it is worth explaining the terms singlet and triplet states. These two terms represent the multiplicity of the spin vector and is equal to  $2S + 1$ , where  $S$  is the total spin quantum number. For an arrangement of two opposite spins ( $s_1 = 1/2$  and  $s_2 = -1/2$ ), the value of  $S$ , which is equal to  $s_1 + s_2$ , is zero. Hence multiplicity is one. Such an arrangement will be represented by a single wave function and thus gives rise to a singlet state. For an arrangement of two parallel spins (may be  $\alpha$  and  $\alpha$  or  $\beta$  and  $\beta$ ), the value of  $S$  is 1 and hence the multiplicity is three. This corresponds to the three different orientations of the total spin angular momentum vector with  $z$ -components equal to  $+1(h/2\pi)$ ,  $0(h/2\pi)$  and  $-1(h/2\pi)$ . Thus, the arrangement of two parallel spins can be represented by the three degenerate wave functions (one for each value of  $m_s$ ) and gives rise to a triplet state. In general, the energy of the triplet state is slightly smaller than the corresponding singlet state. Physically, this can be explained from the fact that each electron is associated with a tiny magnet. In an arrangement of parallel spins, the electrons will be farther apart in space (because of repulsion between the similar orientations of tiny magnets) than in the arrangement of opposite spins. Hence, the electronic repulsion in the triplet state is smaller than that in the singlet state. Consequently, the triplet state has smaller energy than the singlet state.

Quantum mechanically, the *allowed electronic transitions* are those in which spin of electron is preserved. A transition in which spin is reversed is a forbidden transition. Thus, singlet-singlet and triplet-triplet transitions are allowed whereas singlet-triplet transitions are forbidden. In some molecules, singlet-triplet transition becomes weakly allowed due to the fact that the spin-orbit interaction between the heavy atoms of a molecule can reverse the relative orientation of pair of electrons.



## Phosphorescent Spectrum

Now the mechanism of phosphorescence may be explained. The absorption of a photon induces the singlet to singlet transition. In the excited singlet state some of the vibrational energy is lost as the thermal energy due to the intermolecular collisions. When the excited molecule attains the vibrational quantum number where at the extreme of vibration (or at a point where probability of finding the vibrating molecule is large) the geometry of the molecule corresponds to the crossing point of the two energy curves (singlet and triplet), the molecule can cross over from the singlet to triplet state. In triplet state, it continues to exhibit radiationless decay till it has reached the ground vibrational level. Now the molecule cannot radiate its energy because a return to the ground electronic state involves a forbidden transition. But because of spin-orbit coupling, this selection rule is slightly relaxed and thus emission may last long after the original excited state is formed. The above mechanism is in accord with the experimental facts, viz., phosphorescence is more intense in solid samples (as the molecule gets sufficient time for crossing over from singlet to triplet due to less effective collisions between the molecules and the environment), amount of phosphorescence depends on the presence of heavy atoms (which helps breaking the selection rule) and acquiring the magnetic properties by the excited state (due to the presence of the unpaired electron spins).

Finally, the phenomenon of fluorescence or phosphorescence may be compared with the Raman effect. In both cases, red shift is observed. In the former, an electronic excitation is induced whereas in the latter no such excitation is induced. In fluorescence and phosphorescence, the excited electronic state is formed but in Raman effect, the energy is merely transferred from the radiation to molecule and only instantaneous complex is formed.

## Dissipation of Energy from the Excited States

In the end, a few facts regarding the molecular spectra and the dissipation of energy from the electronically excited state may be mentioned. In general, we have

$$\text{Period of rotation} \approx 10^{-11} \text{ s or } 10^{-12} \text{ s}$$

$$\text{Period of vibration} \approx 10^{-13} \text{ s or } 10^{-14} \text{ s}$$

$$\text{Average time between two molecular collisions in the gaseous state} \\ (p \approx 1 \text{ atm}) = 10^{-10} \text{ s}$$

$$\text{Average time between two molecular collisions in the liquid} \\ \text{phase} = 10^{-13} \text{ s}$$

The following conclusions may be drawn from the above data.

- In the gaseous phase, a molecule can execute many rotations and vibrations between two successive molecular collisions. It is because of this reason, the electronic spectra in the gaseous phase is usually accompanied by the coarse structure (due to the vibrational transitions) and the fine structure (due to the rotational transitions).
- In the liquid phase, a molecule does not complete its one complete rotation between the two successive molecular collisions. In other words, the molecule is not free to rotate in the liquid phase. It is because of this, the rotational fine structure in the vibrational or electronic spectrum is usually absent when the spectrum is recorded in the liquid phase.

- The dissipation of rotational energy by the nonradiative process is relatively easy. Most of molecular collisions are in fact effective in exchange of such energy.
- The dissipation of vibrational energy by the nonradiative process is not so easy. On an average,  $10^4$  collisions are required for the transfer of excess vibrational energy as the rotational and translational energy. The life time of a vibrationally excited molecule is thus of the order of  $10^{-9}$  s ( $10^4$  collisions  $\times 10^{-13}$  s collision $^{-1}$ ). This time is much larger than the period of vibration ( $10^{-13}$  s), and hence, a molecule completes many vibrational cycles before it is deactivated.
- When during the vibrational deactivation, the molecule is reached to the lowest vibrational level of the excited electronic state, it is highly improbable that the electronic deactivation, whereby the molecule comes back to the ground-state electronic configuration, takes place in a single collision. The only alternative is that the molecule comes back to the ground-state electronic configuration via a radiative process, i.e. the emission of energy as radiation (phenomenon of fluorescence) occurs.
- During the vibrational deactivation, the molecule may cross over from one potential-energy curve to another if the two curves cross each other. Two types of crossing are possible; (i) where the number of paired or unpaired electrons remain the same, e.g. singlet to singlet or triplet to triplet, and (ii) the number of paired or unpaired electrons differ, e.g. singlet to triplet or triplet to singlet. Transitions involving singlet to singlet or triplet to triplet are quantum mechanically allowed whereas those involving singlet to triplet or vice versa are forbidden. In some molecules, the singlet-triplet transition is weakly allowed due to the spin-orbit interaction between the heavy atoms of the molecules. The crossing over of the molecule from singlet to singlet or triplet to triplet is known as *internal conversion* whereas that from singlet to triplet or vice versa is known as *intersystem crossing*.
- A molecule may dissipate its entire excited electronic and vibrational energy by the nonradiative process if there exists a number of electronic arrangements whose potential energy curves cross one another and also the potential energy curve of the lowest excited electronic state crosses that of the ground electronic state. In the excited electronic state, the vibrational energy is dissipated and in the region where two potential energy curves intersect, an internal conversion takes place where the molecule is moved to the new electronic excited state. In this new state, vibrational deactivation is continued till another crossing of two electronic states is reached. Here again internal conversion occurs followed by the vibrational deactivation. This process of internal conversion and vibrational deactivation is continued till the molecule is reached to the ground electronic state.
- The energy dissipation by nonradiative process is very much affected by the factors which change the frequency of molecular collisions. One of the factors is the temperature of the system. In fact, the energy dissipation by nonradiative process may be replaced by the radiative process if the temperature of the system is very much lowered.

**Example 4.9.1**

The absorption spectrum of  $I_2$  vapour consists of a series of bands which terminate in continuous absorption at 499.5 nm.  $I_2$  molecule in the upper state dissociates into an atom in its ground state and one with an excitation energy of  $90.79 \text{ kJ mol}^{-1}$ . (a) Calculate the dissociation energy of  $I_2$  in its ground electronic state. (b) If the difference between the minima of excited and ground states is  $180.46 \text{ kJ mol}^{-1}$ , what is the dissociation energy in the excited state?

**Solution**

(a) Energy of a photon of wavelength 499.5 nm

$$= \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{(499.5 \times 10^{-9} \text{ m})} = 3.977 \times 10^{-19} \text{ J}$$

Excitation energy of I atom

$$= \frac{90.79 \times 10^3 \text{ J mol}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}} = 1.507 \times 10^{-19} \text{ J}$$

Dissociation energy of  $I_2$  molecule in its ground electronic state

$$= 3.977 \times 10^{-19} \text{ J} - 1.507 \times 10^{-19} \text{ J} = 2.47 \times 10^{-19} \text{ J}$$

Dissociation energy of 1 mol of  $I_2$

$$= (2.47 \times 10^{-19} \text{ J})(6.023 \times 10^{23} \text{ mol}^{-1}) = 1.488 \times 10^5 \text{ J mol}^{-1} = 148.8 \text{ kJ mol}^{-1}$$

(b) Dissociation energy per mol in the excited state

$$\begin{aligned} &= \text{Energy of 1 mol of } 499.5 \text{ nm photons} - \text{Energy difference between the} \\ &\quad \text{minima of excited and ground states} \\ &= (3.977 \times 10^{-19} \text{ J})(6.023 \times 10^{23} \text{ mol}^{-1}) - 180.46 \times 10^3 \text{ J mol}^{-1} \\ &= 59.08 \times 10^3 \text{ J mol}^{-1} = 59.08 \text{ kJ mol}^{-1} \end{aligned}$$

**Example 4.9.2**

Find the kinetic energy of the hydrogen atom produced by photo-dissociation of hydrogen bromide with light of 253.7 nm wavelength. The bond dissociation energy of HBr is equal to  $364 \text{ kJ mol}^{-1}$ . Assume the bromine atom to be in its ground electronic state.

Energy carried by a photon of wavelength 253.7 nm

$$= \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{(253.7 \times 10^{-9} \text{ m})} = 7.830 \times 10^{-19} \text{ J mol}^{-1}$$

Energy required to break one bond of HBr

$$= \frac{(364 \times 10^3 \text{ J mol}^{-1})}{6.023 \times 10^{23} \text{ mol}^{-1}} = 6.044 \times 10^{-19} \text{ J}$$

Kinetic energy of H atom

$$= 7.830 \times 10^{-19} \text{ J} - 6.044 \times 10^{-19} \text{ J} = 1.786 \times 10^{-19} \text{ J}$$

**Example 4.9.3**

(i) The values of  $\nu_e$  in the ground and one of the electronically excited states of a diatomic molecule are  $1641.4 \text{ cm}^{-1}$  and  $1788.2 \text{ cm}^{-1}$ , respectively, and those of  $x_e$  are  $7.11 \times 10^{-3}$  and  $9.19 \times 10^{-3}$ , respectively. Determine the values of vibrational quantum

numbers which will lead to the dissociation of the molecule in the ground and excited states. What are the values of dissociation energies?

(ii) The electronic spectrum of this diatomic molecule involving the above two electronic states includes  $\tilde{\nu}_{00}$  line at  $19378 \text{ cm}^{-1}$  and a convergence limit at  $39231 \text{ cm}^{-1}$ . The dissociation is into one ground state atom and one excited atom with the excitation energy corresponding to  $10308 \text{ cm}^{-1}$ . Calculate the dissociation energies of the two states and compare with those obtained in part (i). Explain any discrepancy.

(iii) Do you expect the molecule to exhibit radiationless decay when it comes back from the excited state to the ground state?

(i) The expression for the vibrational quantum number leading to the dissociation of the molecule is

$$\nu_{\max} = \frac{1}{2x_e} - \frac{1}{2}$$

Hence

$$\nu_{\max}(\text{ground state}) = \frac{1}{2 \times 7.11 \times 10^{-3}} - \frac{1}{2} = 70.32 - 0.5 \approx 70$$

$$\nu_{\max}(\text{excited state}) = \frac{1}{2 \times 9.19 \times 10^{-3}} - \frac{1}{2} = 54.41 - 0.5 \approx 54$$

The expression for  $V_{\max}$  is

$$V_{\max} = \frac{h\nu_e}{4x_e} = \frac{hc\tilde{\nu}_e}{4x_e}$$

Hence

$$\begin{aligned} V_{\max}(\text{ground state}) &= \frac{(6.626 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m s}^{-1})(1641.4 \times 10^2 \text{ m}^{-1})}{4(7.11 \times 10^{-3})} \\ &= 1.147 \times 10^{-18} \text{ J} \end{aligned}$$

$$\begin{aligned} V_{\max}(\text{excited state}) &= \frac{(6.626 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m s}^{-1})(1788.2 \times 10^2 \text{ m}^{-1})}{4(9.19 \times 10^{-3})} \\ &= 9.670 \times 10^{-19} \text{ J} \end{aligned}$$

The expression for  $V_0$  is

$$V_0 = \frac{1}{2}h\nu_e \left(1 - \frac{x_e}{2}\right) = \frac{1}{2}hc\tilde{\nu}_e \left(1 - \frac{x_e}{2}\right)$$

Thus

$$\begin{aligned} V_0(\text{ground state}) &= \frac{1}{2}(6.626 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m s}^{-1}) \\ &\quad \times (1641.4 \times 10^2 \text{ m}^{-1}) \left(1 - \frac{1}{2} \times 7.11 \times 10^{-3}\right) \\ &= 1.628 \times 10^{-20} \text{ J} \end{aligned}$$

$$\begin{aligned} V_0(\text{excited state}) &= \frac{1}{2}(6.626 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m s}^{-1}) \\ &\quad \times (1788.2 \times 10^2 \text{ m}^{-1}) \left(1 - \frac{1}{2} \times 9.19 \times 10^{-3}\right) \\ &= 1.765 \times 10^{-20} \text{ J} \end{aligned}$$

$$\text{Now } D = V_{\max} - V_0$$

$$\text{Thus } D(\text{ground state}) = 1.147 \times 10^{-18} \text{ J} - 1.628 \times 10^{-20} \text{ J} = 1.131 \times 10^{-18} \text{ J}$$

$$D(\text{excited state}) = 9.670 \times 10^{-19} \text{ J} - 1.765 \times 10^{-20} \text{ J} = 9.496 \times 10^{-19} \text{ J}$$

For one mole of the substance, we will have

$$D(\text{ground state}) = (6.023 \times 10^{23} \text{ mol}^{-1}) (1.131 \times 10^{-18} \text{ J})$$

$$= 6.811 \times 10^5 \text{ J mol}^{-1} = 681.1 \text{ kJ mol}^{-1}$$

$$D(\text{excited state}) = (6.023 \times 10^{23} \text{ mol}^{-1}) (9.496 \times 10^{-19} \text{ J})$$

$$= 5.719 \times 10^5 \text{ J mol}^{-1} = 571.9 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \text{(ii) } \tilde{D}(\text{ground state}) &= \tilde{V}(\text{continuum}) - \tilde{V}(\text{excitation energy of the atom}) \\ &= 39\,231 \text{ cm}^{-1} - 10\,308 \text{ cm}^{-1} \\ &= 28\,923 \text{ cm}^{-1} \end{aligned}$$

$D(\text{ground state})$  per mole of the substance is

$$\begin{aligned} N_A(hc\tilde{D}) &= (6.023 \times 10^{23} \text{ mol}^{-1}) (6.626 \times 10^{-34} \text{ J s}) \\ &\quad \times (3 \times 10^8 \text{ m s}^{-1}) (28\,923 \times 10^2 \text{ m}^{-1}) \\ &= 3.463 \times 10^5 \text{ J mol}^{-1} = 346.3 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \tilde{D}(\text{excited state}) &= \tilde{V}(\text{continuum}) - \tilde{V}_{00} \\ &= 39\,231 \text{ cm}^{-1} - 19\,378 \text{ cm}^{-1} \\ &= 19\,853 \text{ cm}^{-1} \end{aligned}$$

$D(\text{excited state})$  per mole of the substance is

$$\begin{aligned} N_A(hc\tilde{D}) &= (6.023 \times 10^{23} \text{ mol}^{-1}) (6.626 \times 10^{-34} \text{ J s}) \\ &\quad \times (3 \times 10^8 \text{ m s}^{-1}) (19\,853 \times 10^2 \text{ m}^{-1}) \\ &= 2.377 \times 10^5 \text{ J mol}^{-1} = 237.7 \text{ kJ mol}^{-1} \end{aligned}$$

Comparison of these values with those obtained in Part (i) reveals that the former are much less than the latter. This is due to the fact that the energy expression is not exact as it does not include higher anharmonicity constants.

$$\begin{aligned} \text{(iii) We have } \tilde{D}(\text{ground state}) &= 28\,923 \text{ cm}^{-1} \\ \tilde{V}_{00} &= 19\,378 \text{ cm}^{-1} \end{aligned}$$

Since  $\tilde{V}_{00} < \tilde{D}(\text{ground state})$ , it is expected that many of the vibrational levels of the excited state will overlap with those of the ground state. Thus, during the vibrational deactivation in the excited state, the molecule can switch over to the vibrational levels of the ground state. Hence, the molecule can come back from the excited state to the ground state via radiationless decay.

## REVISIONARY PROBLEMS

### Nuclear Magnetic Resonance Spectroscopy

- 4.1 (a) What do you mean by magnetic active and inactive nuclei?  
 (b) State whether the spin quantum number is zero, integral or half integral for nuclei having the following characteristics.  
 (i) Both charge and mass even.  
 (ii) Odd charge and even mass.  
 (iii) Even charge and odd mass.  
 (iv) Odd charge and odd mass.  
 (c) What do you mean by the space quantization of angular momentum vector?
- 4.2 (a) Ampere's law is

$$\mu = iA$$

Making use of the above law, derive the relation

$$\mu = \left( \frac{e}{2m_p} \right) L$$

where the various symbols have their usual meaning.

- (b) Quantum mechanical expression of magnetic moment vector is

$$\mu = g \mu_N \sqrt{I(I+1)}$$

Derive the above expression from the expression of  $\mu$  given in Part (a). What is the value of  $\mu_N$  for a proton?

- 4.3 (a) Show that the potential energy of a proton in the presence of a magnetic field is given by

$$V = -B\mu_N g m_I$$

- (b) How does the potential energy of a proton vary in increasing magnetic field?

- (c) The value of  $g$  for proton is 5.585. Calculate the energy difference between two levels of protons in a field of 10 000 gauss. In what range of the electromagnetic radiation does the above energy difference lie?

- 4.4 With the energy difference between the two levels of protons in a magnetic field of 10 000 gauss and using the Boltzmann distribution

$$n_{-1/2}/n_{+1/2} = \exp(-\Delta V/kT)$$

- (i) Calculate the relative population of protons at 300 K.  
 (ii) At what temperature will the upper level be more populated than the lower level? Is there any significance of this temperature?  
 (iii) Do you expect any NMR signal when both levels are equally populated?  
 4.5 Why does the magnetic moment vector execute Larmor precession instead of alignment along the magnetic field?  
 4.6 (a) Explain the following terms with adequate illustrations.

- (i) Chemical shift  
 (ii) Spin-spin interaction  
 (b) Explain, how chemical shift and spin-spin interaction vary with (i) temperature, and (ii) magnetic field.

(c) The PMR signal of a proton depends upon its environments. A less shielded proton shows the signal at low-end field and more highly shielded proton at the high-end field. Explain the above statement taking the example of  $\text{ClCH}_2\text{CCl}_2\text{CH}_3$ .

(d) Explain why TMS,  $(\text{CH}_3)_4\text{Si}$ , is used as one of the internal references in the measurement of chemical shifts of protons.

(e) What are the  $\delta$ - and  $\tau$ -scales?

4.7 (a) Describe the expected low resolution and high resolution spectra of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{CH}_2\text{OH}$ .

(b) Discuss the spectrum of  $\text{CH}_3\text{CH}_2\text{OH}$  in acidic medium.

(c) Describe the spectrum of  $\text{CH}_3\text{CH}_2\text{OH}$  in the presence of  $\text{D}_2\text{O}$ .

4.8 Comment upon the following:

(a) Though the NMR spectrum is recorded at constant radiation frequency and by varying the external magnetic field, yet in most of cases, the chemical shifts are often reported in the unit of frequency, i.e. Hz.

(b) The spin-spin interactions are intramolecular interactions.

(c) A complicated PMR spectrum in the low magnetic field is often simplified if the spectrum is recorded in the high magnetic field.

(d) Chemical shifts are dependent whereas spin-spin interactions are independent of the external magnetic field.

(e)  $^{13}\text{C}$  and  $^{16}\text{O}$  do not exhibit NMR spectra.

4.9 (a) The potential energy of an electron in a magnetic field is given by

$$V = g\mu_B B m_s$$

Derive the above relation.

(b) Calculate: (i) The value of Bohr magneton. (ii) Energy difference between the two levels of an electron in a magnetic field of 3 000 gauss. In what range of the electromagnetic radiation does this energy difference lie?

(c) Using the Boltzmann distribution and the above energy difference between the two levels of electron, calculate the relative distribution of electrons in the two levels.

4.10 The interaction of the unpaired electron with the magnetic active protons of molecule produces hyperfine structures in the ESR spectrum. If there are  $n$  protons in a molecule and if they are equally coupled with the electron, then:

(i) How many lines will be observed in the ESR spectrum?

(ii) How are the relative intensities of these lines related to each other?

4.11 (a) Quantum mechanical expression of rotational energy levels is

$$E = \frac{h^2}{8\pi^2 I} J(J+1)$$

where the various terms have their usual meanings. Show that the above expression can be derived by introducing the appropriate quantum mechanical restriction to the corresponding classical expression of energy.

(b) Show that the degeneracy of various rotational levels is given by the factor  $(2J+1)$ .

4.12 (a) Explain, why many of the lower rotational levels are thickly populated.

(b) Show that the rotational level whose quantum number is given by the expression

$$J = \sqrt{\frac{1}{2} \left( \frac{KT}{h\nu} \right)} - \frac{1}{2}$$

has a maximum population.

(c) Show that the rotational frequency is equal to  $(h/4\pi^2 I) \sqrt{J(J+1)}$ .

4.13 Explain, why only molecules having permanent dipole moment exhibit rotational spectra.

4.14 (a) What are the selection rules for the rotational transitions of a diatomic molecule?

(b) Describe the general appearance of rotational spectrum of a diatomic molecule.

(c) What information can be derived from a rotational spectrum?

4.15 Derive the following classical expression for the frequency of harmonic vibration of a diatomic molecule.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k_f}{\mu}}$$

where the symbols have their usual meanings.

4.16 (a) Show that the classical expression of potential energy of harmonic vibration of a diatomic molecule is given by

$$V = (1/2) k_f (x_2 - x_1)^2$$

where  $x_2$  and  $x_1$  are the displacements of the two atoms from their equilibrium positions.

(b) Since  $x_2 - x_1$  can have any value, the potential energy is a continuous function of displacement. Does this statement hold good for a diatomic molecule? Explain.

4.17 (a) Quantum mechanical expression of potential energy of a harmonic vibration of a diatomic molecule is

$$V = (v + 1/2) h \nu_{\text{classical}}$$

where  $v$  is the vibrational quantum number. What are the permitted values of  $v$ ?

(b) What is zero-point energy? Is it consistent with the uncertainty principle?

(c) Explain, why only the lowest vibrational level is thickly populated.

(d) Explain, why only those molecules for which dipole moment varies during the vibration exhibit vibrational spectra.

4.18 (a) What are the selection rules for the vibrational transitions of a diatomic molecule executing harmonic vibrations?

(b) What is the general appearance of vibrational spectrum of a diatomic molecule?

(c) What information can be derived from a vibrational spectrum?

4.19 (a) The vibration of a diatomic molecule is anharmonic in nature. One of the potential energy expressions in use is the Morse potential expression:

$$E = D_{\text{eq}} [1 - \exp\{\alpha(r_{\text{eq}} - r)\}]^2$$

Draw the typical diagram of potential energy of a diatomic molecule and compare it with that of a classical vibrator.

(b) The energy expression of a molecule exhibiting anharmonic potential of Morse is given by

$$E = \left( v + \frac{1}{2} \right) h\nu_e \left\{ 1 + \left( v + \frac{1}{2} \right) x_e \right\}$$

where  $\nu_e$  is known as equilibrium oscillation frequency of the anharmonic oscillator and  $x_e$  is the corresponding anharmonic constant. Show that the energy difference between the two nearest levels is given by

$$\Delta E = h\nu_e (1 - 2x_e (1 + v''))$$

and hence show that the difference  $\Delta E$  decreases with increasing value of vibrational quantum number.

- (c) What are the selection rules for an anharmonic vibrator?
- (d) Explain, what do you understand by (i) fundamental transition, (ii) overtone transitions, and (iii) hot-bands.
- (e) Show that a diatomic molecule dissociates into atoms if it is present in the vibration state of vibrational quantum number

$$v = \frac{1}{2x_e} - \frac{1}{2}$$

### Vibration-Rotation Spectroscopy

- 4.20 (a) What is the vibration-rotation spectrum of a molecule?
- (b) Explain, why the vibrational and rotational energies can be simply added to give the total energy of a molecule executing simultaneously vibration and rotation motions.
- (c) What are selection rules for the vibration-rotation transitions of a diatomic molecule?
- (d) Show that the wavenumber for the transitions  $v' = 1 \leftarrow v'' = 0$  and  $\Delta J = \pm 1$  is given by

$$\tilde{\Delta E} = \pm 2Bm + \tilde{\nu}_e (1 - 2x_e)$$

where  $m$  can have values, 1, 2, ..., and is given by

$$m = J'' + 1 \quad ; \quad \text{for } \Delta J = +1 \text{ transitions} \\ m = J' + 1 \quad ; \quad \text{for } \Delta J = -1 \text{ transitions}$$

- (e) Draw a typical vibration-rotation spectrum of a diatomic molecule with proper labelling of its P, Q, and R branches.
- (f) What are the essential requirements for a diatomic molecule to exhibit vibration-rotation spectrum? What information can be derived from a vibration-rotation spectrum?

- 4.21 (a) What do you understand by the degrees of freedom of a molecule? How many fundamental vibrations are possessed by a linear and a nonlinear molecule consisting of  $N$  atoms?
- (b) Taking the examples of  $\text{CO}_2$  (linear molecule) and  $\text{H}_2\text{O}$  (nonlinear molecule), illustrate the following vibrational modes: (i) symmetrical stretch, (ii) antisymmetric stretch, (iii) bending.

### Vibrational Spectrum of a Polyatomic Molecule

- (c) Each vibrational mode exhibits its own vibrational spectrum. State how many vibrational lines are expected for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  molecules.
- (d) What do you understand by the group vibrations and skeletal vibrations?
- (e) In general,  $\nu(\text{antisymmetric stretch}) > \nu(\text{symmetric stretch}) > \nu(\text{bending})$ . Explain, the probable reasons for the above fact.
- (f) Explain the following order of group frequencies.

$$\nu(\text{CH}) > \nu(\text{CF}) > \nu(\text{CCl}) > \nu(\text{CBr})$$

$$\nu(\text{C}\equiv\text{C}) > \nu(\text{C}=\text{C}) > \nu(\text{C}-\text{C})$$

- 4.22 (a) What is a Raman spectrum? What is the essential criterion for a molecule to be Raman active?
- (b) How does classical mechanics account for the existence of Raman spectrum?
- (c) What is the explanation of Raman lines from the quantum view point?
- 4.23 (a) What are the selection rules for the pure rotational Raman spectra of diatomic molecules? Hence, show that the Raman lines appear at wavenumbers:

$$\tilde{\nu} = \tilde{\nu}_0 \pm B(4J'' + 6)$$

where  $\tilde{\nu}_0$  is the wave number of Rayleigh line.

- (b) What are the Rayleigh, Stokes and anti-Stokes lines? How do the intensities of Stokes and anti-Stokes lines vary in a pure rotational Raman spectrum?
- 4.24 (a) What are the selection rules for the vibrational Raman spectrum of a diatomic molecule? Show that the fundamental transitions in the Raman spectrum is observed at wave numbers:

$$\tilde{\nu} = \tilde{\nu}_0 \pm \tilde{\nu}_e (1 - 2x_e)$$

- (b) How do the intensities of Stokes and anti-Stokes lines compare with each other in the vibration Raman spectrum?
- 4.25 State the rule of mutual exclusion. Illustrate this by taking typical examples of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

- 4.26 Discuss the following:

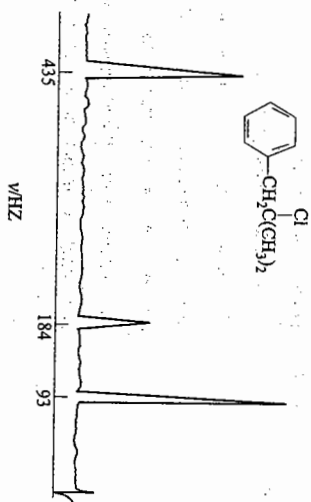
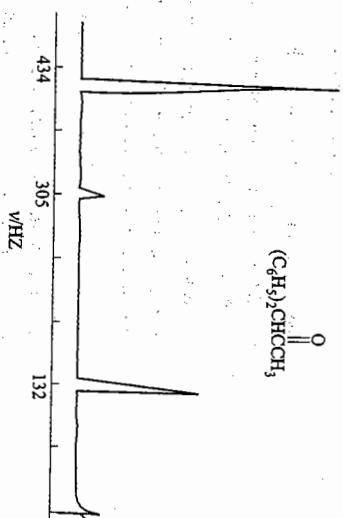
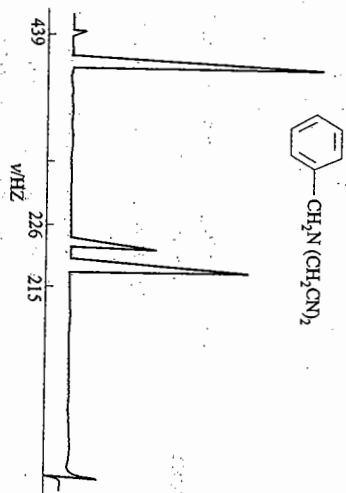
- Franck-Condon principle
- Dissociation and pre-dissociation
- Phosphorescence and fluorescence
- $\sigma \rightarrow \sigma^*$ ,  $\pi \rightarrow \pi^*$  transitions
- Singlet-to-singlet and triplet-to-triplet transitions.
- Singlet-to-triplet transitions are forbidden.

### Electronic Spectroscopy

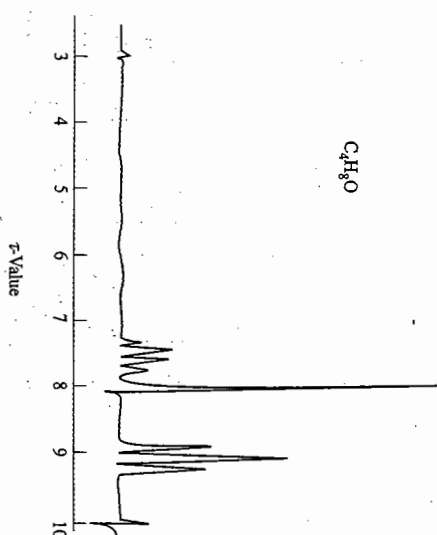
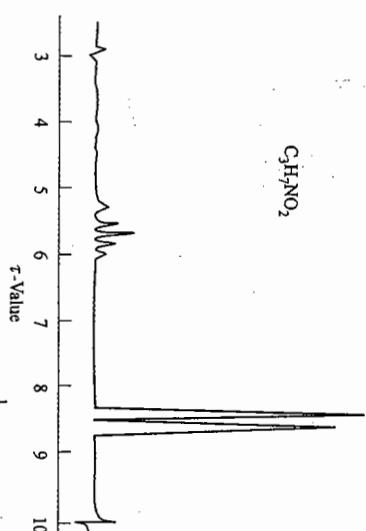
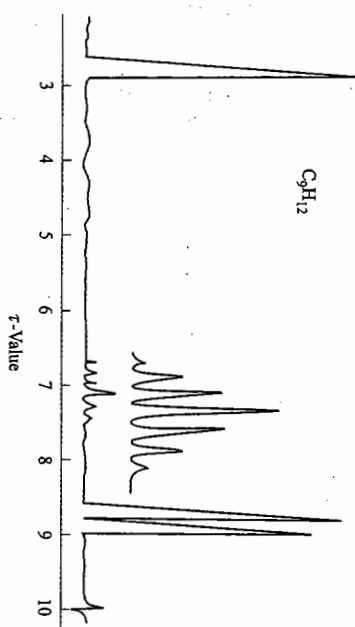
## NMR Spectra

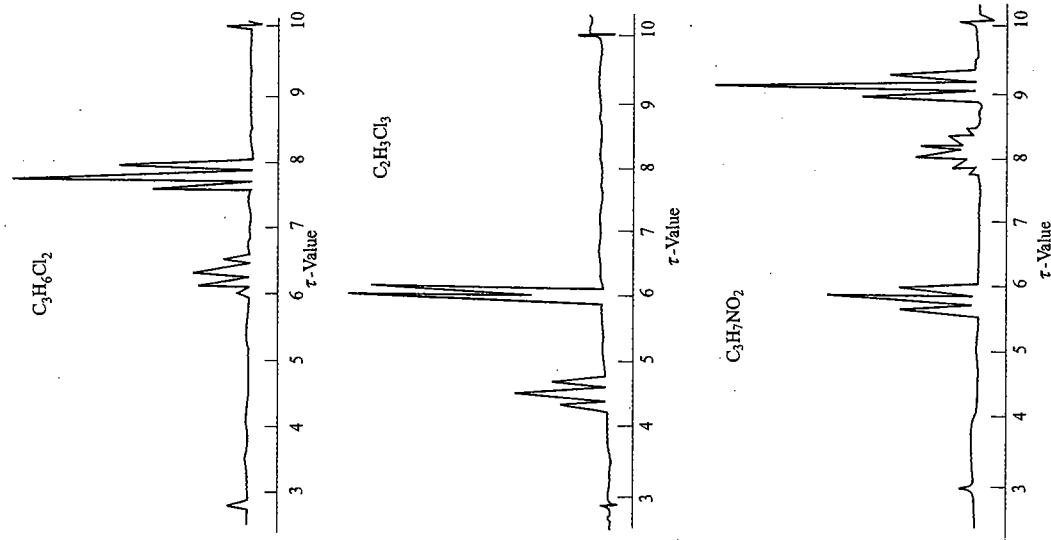
## TRY YOURSELF PROBLEMS

- 4.1 Given below are a few PMR spectra. The molecular structure of the compound is given along with the spectrum. Identify the various peaks in a spectrum with the corresponding hydrogen atoms.



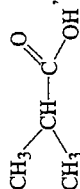
- 4.2 Given below are a few PMR spectra. Identify the structure of the compound whose molecular formula is shown with the diagram.





- 4.3 The infrared spectrum of a compound having the formula  $C_3H_5N$  has no peak at  $3300\text{ cm}^{-1}$ . Predict the NMR spectrum of this compound in terms of the number of peaks expected and their relative intensities.
- 4.4 The NMR spectrum of a compound of molecular formula  $C_6H_9NO$  has two singlet with an intensity ratio of 2 : 1. Identify the compound.
- 4.5 Explain, how to distinguish between the molecules  $CH_3COCH_3$  and  $CH_3CH_2CHO$  on the basis of NMR spectroscopy alone.

- 4.6 Predict the NMR spectrum of diethyl ether.
- 4.7 (a) A compound contains 54.55 mass % carbon, 9.09 mass % hydrogen and 36.36 mass % oxygen. Its NMR spectrum consists of two peaks. The downfield peak is a quartet and is one third as intense as the second peak, which is doublet. Propose a structure for the compound.  
(b) Draw a schematic NMR spectrum of the aromatic compound  $C_6H_5OCH_2CH_3$ .
- 4.8 (a) Explain, why chloroethylene  $CH_2=CHCl$  has three distinct peaks in its NMR spectrum, all of equal intensity.  
(b) Sketch the NMR spectrum for HD molecule.
- 4.9 The NMR spectrum of a compound containing 63.9% carbon, 14.5% hydrogen, and 21.6% oxygen consists of a quartet and a triplet, the latter is 1.5 times as intense as the former. What is the structure of the compound?
- 4.10 (a) The low-resolution spectrum of the compound  $C_6H_8O_2$  exhibits three peaks at 8.1, 5.2 and 1.3 ppm with relative ratio 1, 1 and 6, respectively. Deduce the structure and also draw its expected high-resolution spectrum.

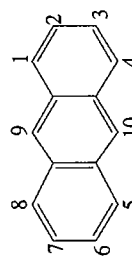


- [Ans. , the peaks at 5.2 and 1.3 ppm split into seven and two, respectively.]
- (b) The low-resolution NMR spectrum of the compound  $C_5H_{10}O$  exhibits two peaks with relative intensities of 2 and 3, respectively. Deduce the structure and also draw its expected high-resolution spectrum.

[Ans.  $CH_3CH_2COCH_2CH_3$ , the peak at low-field end splits into four and that at high-field end into three.]

### ESR Spectroscopy

- 4.11 (a) How many lines will be observed in the ESR spectrum of benzene anion radical. What will be their relative intensities?  
(b) The ESR spectrum of  $C_3H_7$  radical showed 14 absorption peaks with relative intensities of 1, 1, 6, 6, 15, 15, 20, 20, 15, 6, 6, 1 and 1. Is this *n*-propyl or an isopropyl radical?  
[Hint: Use Eq. 4.3.10; *n*-propyl:  $3 \times 3 \times 4$ ; isopropyl: 14 peaks ( $2 \times 7$ )]
- (c) How many ESR peaks are expected for ethyl radical? [Ans. 12 peaks]
- 4.12 Sketch the ESR spectrum of cyclopentadienyl radical  $\cdot C_5H_5$ .
- 4.13 For anthracene negative ion, the hyperfine splitting constants are  $|a_1| = 2.7\text{ G}$ ,  $|a_2| = 1.5\text{ G}$  and  $|a_9| = 5.3\text{ G}$  where numbering goes as follows.



- Predict the ESR spectrum of this ion.
- 4.14 How many ESR absorption lines do you expect for triphenylmethyl radical. [Ans. 196 lines]



**Rotational Spectra**

- 4.15 Explain with examples the effect of thermal energy on the general appearance of the (i) rotational spectra, (ii) vibrational spectra, and (iii) Raman spectra.
- 4.16 Derive the expression of moment of inertia for OCS molecule.

[Ans.  $I = m_{\text{O}}^2 r_{\text{CO}}^2 + m_{\text{S}}^2 r_{\text{CS}}^2 - (m_{\text{O}} r_{\text{CO}} - m_{\text{S}} r_{\text{CS}})^2 / M$ , where  $M = m_{\text{O}} + m_{\text{C}} + m_{\text{S}}$ ]

- 4.17 Is it possible to distinguish between linear and nonlinear molecules from the vibration-rotation spectra?

- 4.18 How will you distinguish between the overtones and hot bands of a spectrum?
- 4.19 Classify the following molecules into different categories exhibiting pure rotational, pure vibrational, vibrational-rotational, rotational Raman and vibrational Raman spectra.

$\text{H}_2$ ,  $\text{HCl}$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ .

- 4.20 Tabulated below are the stretching frequencies in  $\text{cm}^{-1}$  of some of the bonds.
- $\text{OH}$  3 700 ;  $\text{NH}$  3500 ;  $\text{CH}$  3 000 ;  $\text{SH}$  2 600 ;  $\text{PH}$  2 400

Explain the relative frequencies in terms of bond characteristics.

- 4.21 Figure 4.5.2 depicts the plot of  $\nu$  versus  $\Delta x$ . What type of graph do you expect between  $d\nu/d(\Delta x)$  and  $\Delta x$ ? What is its slope?

- 4.22 Why is the stretching vibration frequency of a hydrogen bonded O—H bond lower than that of a free O—H bond?

[Hint: Lengthening of O—H bond due to hydrogen bonding reduces the force constant.]

- 4.23 Justify the following statements:

(a) The vibrational structure of the electronic absorption spectrum is characteristic of the higher electronic level whereas that of fluorescence spectrum is characteristic of the lower electronic state.

(b) Fluorescence or phosphorescence radiation has a lower frequency than the incident radiation.

(c) Phosphorescence is intense from solid samples.

(d) The amount of phosphorescence depends on the presence of a heavy atom.

(e) Fluorescence is favoured in very low pressure.

(f) Phosphorescence unlike fluorescence cannot be studied in the liquid phase.

[Ans. (a) Absorption (emission) involves the transfer of electron from the lowest vibrational level of the lower (upper) electronic state to the various vibration levels of the higher (lower) electronic state. (b) Loss of vibrational energy in the upper electronic state as radiationless decay due to the molecular collisions. (c) Less effective collisions in solid phase give sufficient time for intersystem crossing. (d) Heavy atom helps breaking the selection rule of not allowing singlet-to-triplet transition. (e) Less collisions at low pressure decreases the chances of radiationless decay. (f) During the time required for intersystem crossing, a large number of collisions that take place increases the chances of radiationless decay and decreases the chances of intersystem crossing.]

- 4.24 The energy of  $n$ ,  $\pi$  and  $\pi^*$  orbitals of  $\alpha\beta$ -unsaturated carbonyl compounds are lowered in a more polar solvent due to the solvation effects. The effects produced are

$$(\Delta E)_n \gg (\Delta E)_{\pi^*} > (\Delta E)_\pi$$

Predict, what effects on  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions are produced if the spectra of these compounds are recorded in the solvents of increasing polarity. [Ans. Blue shift (wavelength decreases) for  $n \rightarrow \pi^*$  transitions and red shift (wavelength increases) for  $\pi \rightarrow \pi^*$  transition.]

**Proton Magnetic Resonance****NUMERICAL PROBLEMS**

- 4.1 (a) A particular isotope absorbs energy at the radiofrequency of  $17.3 \times 10^6$  Hz when it is in a magnetic field of one tesla. Calculate the nuclear  $g$  factor for this isotope.

(b) The NMR signal of a compound is found to be 240 Hz downfield from the TMS peak using a spectrometer operating at 60 MHz. Calculate its chemical shift in ppm relative to TMS.

[Ans. (a) 2.310 6 (b) 4 ppm]

(c) A particular NMR instrument operates at 30 256 MHz. What magnetic fields are required to bring a hydrogen nucleus and a  $^{13}\text{C}$  nucleus to resonance at this frequency. Given:  $g(\text{H}) = 5.584$  and  $g(^{13}\text{C}) = 1.1404$

[Ans. H, 0710 T,  $^{13}\text{C}$ , 2.8274 T]

- 4.2 (a) The nucleus  $^{11}\text{B}$  has  $m_I = 3/2$  and  $g_N = 1.792$ . Calculate the energy levels of a  $^{11}\text{B}$  nucleus in a magnetic field of 1.50 T. (b) Calculate the NMR absorption frequency of  $^{11}\text{B}$  in a magnetic field of 1.50 T.

- 4.3 (a) Calculate the relative population difference, i.e.  $(n_B - n_A)/(n_B + n_A)$  for electron spins in a magnetic field at 0.3 T at 300 K.

[Hint: Evaluate  $n_A/n_B$  using Boltzmann equation, add and subtract this quantity in one and then take the ratio.] [Ans. 0.000 675]

(b) Repeat the problem 4.3a for protons. [Ans.  $10^{-6}$ ]

(c) The ESR spectrum of atomic hydrogen was recorded on a spectrometer working at 9 302 GHz. The value of hyperfine coupling constant was found to be 50.7 mT. Find the value of  $B$  at which the two lines of atomic hydrogen will be observed. [Ans. 306.85 mT and 357.55 mT]

(d) Predict the appearance of the ESR spectrum of (a)  $\text{CD}_3$  and (b)  $\text{CH}_3\text{CD}_2$ . [Ans. (a) Quintet of relative intensities 1 : 2 : 3 : 2 : 1 and (b) Quartet (1 : 3 : 3 : 1) of quintets (1 : 2 : 3 : 2 : 1).]

(e) An unpaired electron in the presence of two protons gives the following four line ESR spectrum:  $\Delta B = 0, 1, 3, 4$  G. What are the two coupling constants in G and MHz?

[Ans.  $a_1 = 3$  G or 8.40 MHz,  $a_2 = 1$  G or 2.80 MHz]

**Rotational Spectrum**

- 4.4 The separation between successive lines of the rotational spectrum of a diatomic molecule is 20  $\text{cm}^{-1}$ . Calculate:

(a) The moment of inertia of the molecule.

(b) Rotational frequency and the period of rotation for the rotational quantum number 1.

(c) Relative population of molecules in the rotational states  $J = 0, 3$  and 6 at 300 K with respect to that of  $J = 0$ .

(d) Which rotational energy level has the highest population.

- 4.5 The vibrational spectrum of a linear molecule shows two strong absorptions at 727  $\text{cm}^{-1}$  and 3270  $\text{cm}^{-1}$ , two absorptions of medium intensity at 1 433  $\text{cm}^{-1}$  and 2 085  $\text{cm}^{-1}$  and two weak absorptions at 1 370  $\text{cm}^{-1}$  and 2 800  $\text{cm}^{-1}$ . Suggest assignment of these absorptions.

**Vibrational Spectrum**



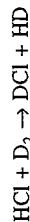
4.6 The vibrational energy levels of  $I_2$  molecule is given by the expression

$$\tilde{E}_v/\text{cm}^{-1} = 215 \left( v + \frac{1}{2} \right) \left\{ 1 - 0.003 \left( v + \frac{1}{2} \right) \right\}$$

where  $v$  is the vibrational quantum number.

Calculate: (a) The force constant of the molecule. (b) The anharmonicity constant. (c) Zero-point energy. (d) Fundamental vibrational frequency. (e) The frequency of first overtone. (f) The period of vibration in the lowest vibrational level. (g) The number of molecules in the level  $v = 1$  relative to  $v = 0$  level at 500 K. (h) The value of vibrational quantum number which leads to the dissociation of the molecule. (i) The dissociation energy of the  $I_2$  molecule. Do you expect it to be overestimated?

4.7 The vibrational wavenumbers of the following molecules in their  $v = 0$  are  $\text{HCl}$ :  $2\,885\text{ cm}^{-1}$ ;  $\text{DCI}$ :  $1\,990\text{ cm}^{-1}$ ;  $\text{D}_2$ :  $2\,990\text{ cm}^{-1}$ ; and  $\text{HD}$ :  $3\,637\text{ cm}^{-1}$ . Calculate the energy change, in  $\text{kJ mol}^{-1}$  of the reaction.



$$[\text{Hint: } \Delta\tilde{E} = \tilde{v}_0(\text{DCI}) + \tilde{v}_0(\text{HD}) - \tilde{v}_0(\text{HCl}) - \tilde{v}_0(\text{D}_2)]$$

$$[\text{Ans. } -2.967\text{ kJ mol}^{-1}]$$

4.8 Compare the force constants for the bond strengths in  $\text{CN}$  and  $\text{CN}^+$  if  $\tilde{v}_e = 2\,068.61\text{ cm}^{-1}$  and  $1\,580\text{ cm}^{-1}$ , respectively. Interpret the results on the basis of electronic configurations.

4.9 To what temperature must we heat a diatomic gas at  $298\text{ K}$  to excite one per cent of its molecules to the first excited state of vibration energy level? The fundamental vibrational frequency of the gas is  $1\,545\text{ cm}^{-1}$ . [Ans.  $482.4\text{ K}$ ]

4.10 The first four vibrational energy levels of  $\text{HCl}$  were found to lie at  $2\,885.9$ ,  $5\,668.0$ ,  $8\,346.9$ ,  $10\,923.1\text{ cm}^{-1}$  with respect to the ground state. With the help of these data, calculate the anharmonicity constant, zero-point energy and the dissociation energy of the molecule. [Ans.  $\text{DE} = 5.14\text{ eV}$ ]

4.11 The force constant for  $^2\text{D}^{35}\text{Cl}$  is  $4.903 \times 10^5\text{ dyn cm}^{-1}$ . Calculate  $\tilde{\nu}$  of  $v = 0$  state. What is the frequency of vibration of  $\text{DCI}$  in  $v = 0$  state? Is this dependent on  $v$ ? [Ans.  $2\,091\text{ cm}^{-1}$ ,  $6.27 \times 10^{13}\text{ s}^{-1}$ , no]

4.12 The constant  $a$  in the Morse potential (Eq. 4.5.19) is given by the relation

$$a = 4.445 \sqrt{v_e \mu / D}$$

The values of  $\tilde{v}_e$  and  $\tilde{v}_e x_e$  for  $\text{H}_2$  are  $4\,395.24$  and  $118.0\text{ cm}^{-1}$ . Its dissociation energy is  $38\,278\text{ cm}^{-1}$ . Plot the Morse curve for  $\text{H}_2$  and show the spacing of vibrational levels on the graph.

4.13 The Morse potential (Eq. 4.5.19) generates

$$\tilde{V} = \tilde{v}_e \left( v + \frac{1}{2} \right) - \tilde{v}_e x_e \left( v + \frac{1}{2} \right)^2$$

$$\text{if } \tilde{v}_e = 10^{-1} a \left( \frac{hD_e}{2\pi^2 c \mu} \right)^{1/2} \text{ and } \tilde{v}_e x_e = 10^{-2} \frac{ha^2}{8\pi^2 c \mu}$$

where  $D_e$ ,  $\tilde{v}_e$  and  $\tilde{v}_e x_e$  are in  $\text{cm}^{-1}$  while the other quantities are in normal SI units. If  $r_e = 74.17\text{ pm}$ ,  $D_e = 38\,318\text{ cm}^{-1}$ ,  $\tilde{v}_e = 4\,405.3\text{ cm}^{-1}$  and  $\tilde{v}_e x_e = 125.325\text{ cm}^{-1}$  for  $\text{H}_2$ , plot  $U(r) = V(r) - D_e$  against  $r$  showing first four vibrational levels.

[Ans. Minimum at  $74.17\text{ pm}$  and  $-38\,318\text{ cm}^{-1}$  vibrational lines at  $-36\,147$ ,  $-31\,922$   $-28\,088$  and  $-24\,435\text{ cm}^{-1}$ ]

4.14 In the vibration-rotation spectrum of  $\text{H}^{35}\text{Cl}$ , the following absorptions occur. Label the lines and calculate  $B$ ,  $r$ ,  $\tilde{\nu}$  and  $k$  of the molecule.

$\tilde{\nu}/\text{cm}^{-1}$	2 906.3	2 927.5	2 948.7	2 969.9	30 12.23	3 033.4
	3 054.6	3 075.8				

Which of the absorption will have maximum intensity?

[Ans.  $B = 10.6\text{ cm}^{-1}$ ,  $r = 127\text{ pm}$ ,  $\tilde{\nu} = 2\,991\text{ cm}^{-1}$ ,  $k = 5.14 \times 10^5\text{ dyn cm}^{-1}$ ]

4.15 A molecule  $\text{AB}_2$  has the following infrared and Raman spectra:

$\text{cm}^{-1}$	Infrared	Raman
3 756	Very strong	—
3 652	Strong	Strong, polarized.
1 595	Very strong	—

Comment upon the geometry of the molecule and assign the observed lines to the corresponding vibrations.

4.16 If one of the Raman lines appears at  $460\text{ nm}$  when excited by light of wavelength  $435.8\text{ nm}$ , at what frequency will it show absorption in the infrared region?

4.17 The vibrational Raman spectrum of  $^{35}\text{Cl}_2$  shows a series of Stokes lines separated by  $0.9752\text{ cm}^{-1}$ . What is the bond length of  $\text{Cl}_2$ ?

[Ans.  $0.1988\text{ nm}$ ]

4.18 The band spectrum of  $\text{Br}_2$  terminates at a wavelength of  $510.7\text{ nm}$ . The energy of the excited atoms formed in the dissociation is  $43.51\text{ kJ mol}^{-1}$  in excess of that possessed by the neutral atoms. What is the spectroscopic dissociation energy of  $\text{Br}_2$ ? [Ans.  $190.37\text{ kJ mol}^{-1}$ ]

4.19 The dissociation energy of ground electronic state of a diatomic molecule is  $326.35\text{ kJ mol}^{-1}$ . Its first excitation state dissociates with one atom in the ground state and the other in excited state. The energy of excitation of the excited atom is  $209.2\text{ kJ mol}^{-1}$ . What is the maximum wavelength of radiation which will cause the molecule in the ground state to cause dissociation in the excited state? If the difference in the potential energy minima for the two molecular levels is  $2.95 \times 10^6\text{ m}^{-1}$ , what is the dissociation energy of the excited state of the molecule? [Ans.  $223.4\text{ nm}$ ,  $182.42\text{ kJ mol}^{-1}$ ]

4.20 The zero-point energy of the ground state of a molecule is  $1.176 \times 10^5\text{ m}^{-1}$  and that of its lowest excited state is  $7.27 \times 10^4\text{ m}^{-1}$ . The energy difference between the two minima of molecular electronic levels is  $5.0206 \times 10^6\text{ m}^{-1}$ . What is the energy of the electronic excitation from  $v''=0$  level to  $v'=0$  level?

[Ans.  $4.9757 \times 10^6\text{ m}^{-1}$ ]

## Vibration-Rotation Spectrum

## Raman Spectrum

## Electronic Spectrum

4.21 The values of  $\tilde{\nu}_e$  and  $\tilde{\nu}_e x_e$  for upper and lower electronic states of a molecule are 151 561, 1 725 and 217 021 and 1 346  $\text{m}^{-1}$ , respectively. If the difference between the minima of two molecular levels is  $6.50748 \times 10^6 \text{ m}^{-1}$ , calculate the energy of (0, 0)-transition. [Ans.  $6.474655 \times 10^6 \text{ m}^{-1}$ ]

4.22 The absorption spectrum of  $\text{O}_2$  shows vibrational structure which ends with a continuum at  $56\,876 \text{ cm}^{-1}$ , the upper electronic state dissociates into one ground state atom and the other at excited state with the excitation energy of  $15\,875 \text{ cm}^{-1}$ . Estimate the dissociation energy in the ground state.

[Ans.  $4.906 \times 10^5 \text{ J mol}^{-1}$ ]

4.23 Which of the vibrational modes of  $\text{CO}_2$  are IR active? What is the line spacing in the P and R branches of the vibration-rotation spectrum of these vibrational modes?

[Ans. Antisymmetric stretch and bending vibrations. Line spacing is  $4B$  as alternative rotational levels are unoccupied.]

4.24 Which of the vibrational modes of acetylene are IR active? What is the line spacing in the P and R branches of the vibration-rotation spectrum of these vibrational modes?

[Ans. Antisymmetric stretch and one of the bending modes. Line spacing is  $2B$  with intensity variations in the ratio of 3 : 1 due to hydrogen atoms.]

## ANNEXURE

### A Qualitative Study of Quantum Mechanical Treatment of Spin Transitions in AX, $A_2$ and $AX_2$ Systems

The spins of protons in a molecule can be described by the nuclear spin wave functions. For the protons in AX,  $A_2$  and  $AX_2$  systems, the nuclear spin wave functions along with their energies and the possible spin transitions amongst them are described below.

Since the proton can have two nuclear spins ( $m_I = 1/2$  designated as  $\alpha$  spin and  $m_I = -1/2$  designated as  $\beta$  spin), there are four possible magnetic states that correspond to the four possible combinations of the spin quantum numbers of A and X protons. These are shown in Table A.1.

Table A.1 Nuclear Spin Wave Functions for AX System

$m_I(A)$	$m_I(X)$	$m_I(A) + m_I(X)$	Wave function <sup>†</sup>
$\frac{1}{2}$	$\frac{1}{2}$	1	$\psi_{+1} = \alpha(A)\alpha(X)$
$\frac{1}{2}$	$-\frac{1}{2}$	0	$\psi_0 = \alpha(A)\beta(X)$
$-\frac{1}{2}$	$\frac{1}{2}$	0	$\psi'_0 = \beta(A)\alpha(X)$
$-\frac{1}{2}$	$-\frac{1}{2}$	-1	$\psi_{-1} = \beta(A)\beta(X)$

<sup>†</sup> Subscript of wave function  $\psi$  is the value of total magnetic quantum number. The symbol  $\alpha$  and  $\beta$  represent spin wave functions.

The energies of the states shown in Table A.1 can be evaluated as usual by employing the expression

$$E = \frac{\langle \psi | H_{\text{op}} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (\text{A.1})$$

If the two protons in the AX system do not interact with each other, then the energy operator  $H_{\text{op}}$  is simply the sum of energy operators for the individual protons, i.e.

$$H_{\text{op}} = H_{\text{op}}(A) + H_{\text{op}}(X)$$

It can be shown that with the form of wave functions given in Table A.1, the energy of a system is simply the sum of individual energies of protons.

For example, for the function  $\psi_{+1}$ , we have

$$E_1 = \frac{\langle \alpha(A)\alpha(X) | H_{op}(A) + H_{op}(X) | \alpha(A)\alpha(X) \rangle}{\langle \alpha(A)\alpha(X) | \alpha(A)\alpha(X) \rangle} \\ = \frac{\langle \alpha(A) | H_{op}(A) | \alpha(A) \rangle \langle \alpha(X) | \alpha(X) \rangle + \langle \alpha(X) | H_{op}(X) | \alpha(X) \rangle \langle \alpha(A) | \alpha(A) \rangle}{\langle \alpha(A) | \alpha(A) \rangle \langle \alpha(X) | \alpha(X) \rangle} \quad (A.2)$$

Since the spin functions constitute an orthogonal set, we have

$$E_1 = \langle \alpha(A) | H_{op}(A) | \alpha(A) \rangle + \langle \alpha(X) | H_{op}(X) | \alpha(X) \rangle \\ = E_A + E_X$$

The potential energy of a hydrogen atom in a molecule in the presence of a magnetic field is given by

$$E_{m_l} = -m_l \gamma \frac{h}{2\pi} (1 - \sigma) B$$

where  $\sigma$  is the shielding constant of the hydrogen atom and  $\gamma$  is gyromagnetic ratio. The Hamiltonian operator is given by

$$H_{op} = -\gamma B(1 - \sigma) \hat{L}_z$$

where  $\hat{L}_z$  is the operator corresponding to the z-component of angular momentum.

The operation of  $\hat{L}_z$  on the proton spin wave function is represented as

$$\hat{L}_z \alpha = \left\{ m_l \left( \frac{h}{2\pi} \right) \right\} \alpha \quad \text{where } m_l = +1/2$$

$$\hat{L}_z \beta = \left\{ m_l \left( \frac{h}{2\pi} \right) \right\} \beta \quad \text{where } m_l = -1/2$$

Thus, the Schrödinger equation for the proton spins can be written as

$$H_{op} \alpha = \left\{ -\frac{1}{2} \gamma \frac{h}{2\pi} (1 - \sigma) B \right\} \alpha \quad (A.3a)$$

$$H_{op} \beta = \left\{ +\frac{1}{2} \gamma \frac{h}{2\pi} (1 - \sigma) B \right\} \beta \quad (A.3b)$$

Following Eqs (A.2) and (A.3), the energies of the wave functions given in Table A.1 can be derived and are given in Table A.2.

Table A.2 Energies of Wave Functions for AX System

Wave function	Energy
$\psi_{+1} = \alpha(A)\alpha(X)$	$E_{+1} = -\frac{1}{2} \gamma \frac{h}{2\pi} B(1 - \sigma_A) - \frac{1}{2} \gamma \frac{h}{2\pi} B(1 - \sigma_X)$
$\psi_0 = \alpha(A)\beta(X)$	$E_0 = -\frac{1}{2} \gamma \frac{h}{2\pi} B(1 - \sigma_A) + \frac{1}{2} \gamma \frac{h}{2\pi} B(1 - \sigma_X)$
$\psi'_0 = \beta(A)\alpha(X)$	$E'_0 = +\frac{1}{2} \gamma \frac{h}{2\pi} B(1 - \sigma_A) - \frac{1}{2} \gamma \frac{h}{2\pi} B(1 - \sigma_X)$
$\psi_{-1} = \beta(A)\beta(X)$	$E_{-1} = +\frac{1}{2} \gamma \frac{h}{2\pi} B(1 - \sigma_A) + \frac{1}{2} \gamma \frac{h}{2\pi} B(1 - \sigma_X)$

Assuming  $\sigma_A$  to be smaller than  $\sigma_X$ , the relative order of energies are

$$E_{+1} < E_0 < E'_0 < E_{-1}$$

Figure A.1a displays schematically the relative order of energies of the four magnetic states.

The selection rules as derived from quantum mechanics are as follows.

$$\Delta m_l = \pm 1 \text{ for the nucleus undergoing spin transition}$$

$$\Delta m_l = 0 \text{ for the other nuclei}$$

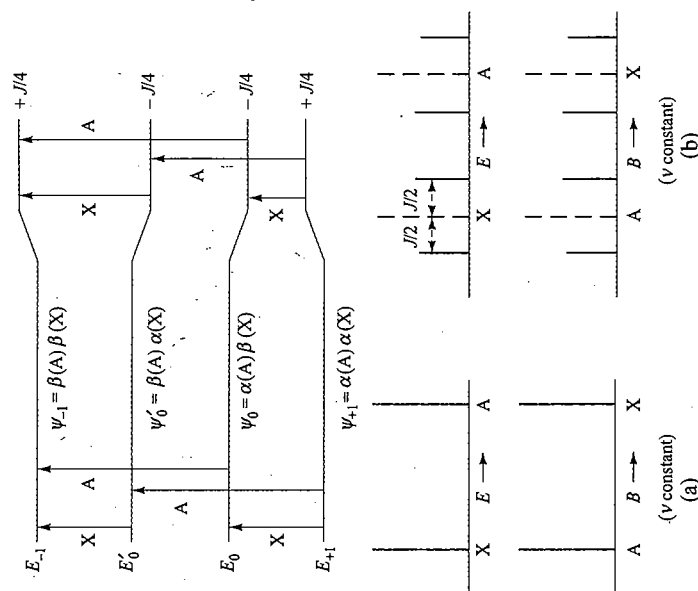


Fig. A.1 Energies of wave functions and allowed spin transitions for system A<sub>2</sub> (a) in the absence of spin-spin interactions, and (b) in the presence of spin-spin interactions

The allowed spin transitions and the associated energy changes are described in Table A.3. These are also shown in Fig. A.1.

Table A.3 Allowed Spin Transitions for the System AX

Proton undergoing transition	Transition	Energy change transition
A	$\psi'_0 \leftarrow \psi_{+1}$	$\gamma \frac{h}{2\pi} B(1 - \sigma_A)$
A	$\psi_{-1} \leftarrow \psi_0$	$\gamma \frac{h}{2\pi} B(1 - \sigma_X)$
X	$\psi_0 \leftarrow \psi_{+1}$	$\gamma \frac{h}{2\pi} B(1 - \sigma_X)$
X	$\psi_{-1} \leftarrow \psi'_0$	$\gamma \frac{h}{2\pi} B(1 - \sigma_A)$

Thus, two transitions at the indicated energy changes are observed as shown at the foot of Fig. A.1a. The chemical shift between the two is

$$\gamma \frac{h}{2\pi} B(\sigma_X - \sigma_A) \quad (\text{A.4})$$

If the spins of protons A and X interact with each other, it is expected that the system of parallel spins ( $\alpha$  and  $\alpha$  or  $\beta$  and  $\beta$ ) will repel each other and that of opposite spins will attract each other. Thus, the systems of parallel spins (i.e. of wave functions  $\psi_{-1}$  and  $\psi_{+1}$ ) will be destabilized whereas those of paired spins (i.e. of wave functions  $\psi_0$  and  $\psi'_0$ ) will be stabilized. If we write the change in energy for each state as  $\pm J/4$  ( $= Jm_A m_X$ ), then the energy diagram is changed as shown in Fig. A.1b. From Fig. A.1b, it also follows that the energies of transitions  $\psi_0 \leftarrow \psi_{-1}$  and  $\psi'_0 \leftarrow \psi_{+1}$  are decreased by  $J/2$  whereas those of  $\psi_{-1} \leftarrow \psi'_0$  and  $\psi_{+1} \leftarrow \psi_0$  are increased by  $J/2$ . The spectrum thus will modify as shown at the foot of Fig. A.1b. Hence, the single resonance lines of A and X protons observed in the absence of spin-spin interactions will each be replaced by two lines. The intensities of the two lines of either A proton or X proton will be half of the parent line observed in the absence of spin-spin interactions.

## The System $A_2$

The best example of  $A_2$  molecule is  $H_2$ . The nuclei in  $H_2$  molecule can have either the same spin ( $\alpha\alpha$  or  $\beta\beta$ ) or different spins ( $\alpha\beta$ ). The different magnetic states of  $H_2$  molecules classified on the basis of total magnetic quantum number are as follows.

1. *Total magnetic quantum number equal to -1* In this state, both the nuclei have  $\beta$  spin. The nuclear wave function describing this state is  

$$\psi_{-1} = \beta(1)\beta(2)$$
2. *Total magnetic quantum number equal to +1* In this stage, both the nuclei have  $\alpha$  spin which is described by the wave function  

$$\psi_{+1} = \alpha(1)\alpha(2)$$
3. *Total magnetic quantum number equal to zero* In this state, one nucleus has  $\alpha$  spin and the other has  $\beta$  spin. Since the two nuclei are indistinguishable, such a situation is described with the linear combinations of spin wave functions  $\alpha(1)\beta(2)$  and  $\beta(1)\alpha(2)$ . Thus, we have

$$\text{Symmetric wave function:} \quad \psi_{0,s} = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\text{Antisymmetric wave function:} \quad \psi_{0,a} = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

where the subscripts s and a stand for the symmetric and antisymmetric nature of the wave function. In the absence of an external field and the spin-spin interactions, all the above four wave functions have the same energies. In the presence of a magnetic field, this degeneracy is removed. The respective energies of the four functions  $\psi_{+1}$ ,  $\psi_{0,s}$ ,  $\psi_{0,a}$  and  $\psi_{-1}$ , as derived by the method describe above, are

$$-\gamma \frac{h}{2\pi} (1 - \sigma)B; \quad 0; \quad 0; \quad +\gamma \frac{h}{2\pi} (1 - \sigma)B;$$

These are shown schematically in Fig. A.2a.

## The System $AX_2$

Quantum mechanically, the spin transitions are allowed only amongst either symmetric or antisymmetric wave functions. The spin transitions from symmetric to antisymmetric wave functions or vice versa are forbidden. Besides the above restriction, the selection rule permits only those transitions for which  $\Delta m_l = \pm 1$  for the proton undergoing transition. Thus, two transitions  $\psi_{0,s} \leftarrow \psi_{+1}$  and  $\psi_{-1} \leftarrow \psi_{0,s}$  are allowed and both of them have the same energy. Hence, the system  $A_2$  produces only one resonance line.

In the presence of spin-spin interactions, the energies of symmetric wave functions are destabilized by the same amount  $+J/4$  whereas that of antisymmetric wave function is stabilized by the amount  $-3J/4$ .<sup>†</sup> The energy diagram shown in Fig. A.2a is modified to the one shown in Fig. A.2b.

Since the transitions only amongst symmetric wave functions are allowed, it is obvious from Fig. A.2b that the energies of allowed transitions  $\psi_{0,s} \leftarrow \psi_{+1}$  and  $\psi_{-1} \leftarrow \psi_{0,s}$  remain the same as those observed in the absence of spin-spin interaction. Thus, the single resonance line observed in the absence of spin-spin interaction remains unaffected in the presence of spin-spin interaction. The above characteristic of destabilization of all symmetric wave functions due to the spin-spin interactions is maintained for any number of chemically equivalent protons. Thus, we conclude that the chemical equivalent protons do not show spin-spin splitting in spite of the fact that they do involve spin-spin interactions.

For the system  $AX_2$ , we have eight magnetic states as described in Table A.4. Let  $\sigma_A$  and  $\sigma_X$  be the shielding constants for protons A and X, respectively, and let we write

$$E_A = \frac{1}{2} \frac{h}{2\pi} (1 - \sigma_A) B \quad (\text{A.5})$$

$$E_X = \frac{1}{2} \frac{h}{2\pi} (1 - \sigma_X) B \quad (\text{A.6})$$

<sup>†</sup> The spin-spin interaction energy is proportional to the scalar product of nuclear spin angular momenta of the two protons, i.e.  $E \propto L_1 \cdot L_2$ . Since the square of the total nuclear spin angular momenta is

$$L^2 = (L_1 + L_2) \cdot (L_1 + L_2) = L_1^2 + L_2^2 + 2L_1 \cdot L_2$$

we can write

$$L_1 \cdot L_2 = (1/2) (L^2 - L_1^2 - L_2^2) = (1/2) [I(I+1) - I_1(I_1+1) - I_2(I_2+1)] (\hbar/2\pi)^2$$

For protons,  $I_1 = I_2 = 1/2$ . Hence

$$L_1 \cdot L_2 = (1/2) [I(I+1) - 3/2] (\hbar/2\pi)^2$$

For the two parallel spins of protons,  $I = 1$ . Hence

$$L_1 \cdot L_2 = (1/2)(2 - 3/2)(\hbar/2\pi)^2 = (1/4)(\hbar/2\pi)^2$$

and thus  $E \propto (1/4)(\hbar/2\pi)^2 = (1/4)J$

For the two antiparallel spins of protons,  $I = 0$ . Hence

$$L_1 \cdot L_2 = (1/2)(0 - 3/2)(\hbar/2\pi)^2 = -(3/4)(\hbar/2\pi)^2$$

and thus  $E \propto -(3/4)(\hbar/2\pi)^2 = -(3/4)J$

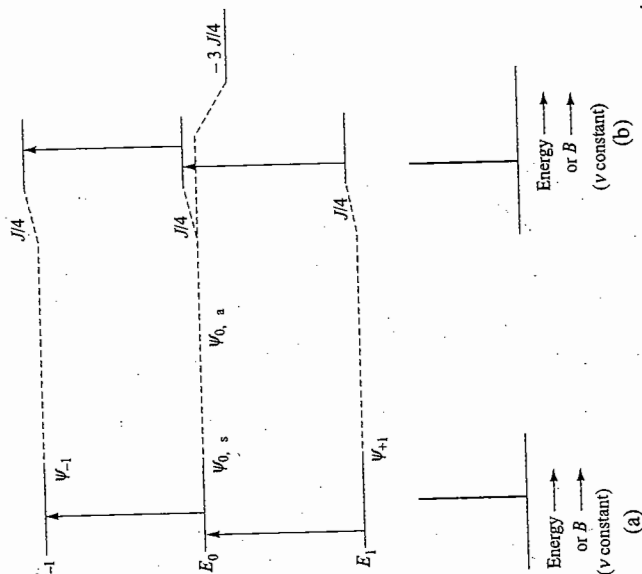


Fig. A.2 Energies of wave functions and allowed spin transitions for the system  $A_2$  (a) in the absence of spin-spin interactions, and (b) in the presence of spin-spin interactions

For the eight magnetic states shown in Table A.4, the energy expressions in the absence of spin-spin interactions can be worked out as usual. These are also included in Table A.4.

Table A.4 Wave Functions and the Corresponding Energies for the System  $AX_2$

Magnetic state	Total magnetic quantum number	Function	Energy
1	$\frac{3}{2} + \frac{1}{2}$	$\alpha\alpha\alpha$	$-E_A - 2E_X$
2	$\frac{1}{2} + \frac{1}{2}$	$\alpha \left\{ \frac{1}{\sqrt{2}} (\alpha\beta + \beta\alpha) \right\}$	$-E_A$
3	$\frac{1}{2} + \frac{1}{2}$	$\alpha \left\{ \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha) \right\}$	$-E_A$
4	$\frac{1}{2} + \frac{1}{2}$	$\beta\alpha\alpha$	$E_A - 2E_X$
5	$\frac{1}{2} - \frac{1}{2}$	$\alpha\beta\beta$	$-E_A + 2E_X$
6	$\frac{1}{2} - \frac{1}{2}$	$\beta \left\{ \frac{1}{\sqrt{2}} (\alpha\beta + \beta\alpha) \right\}$	$E_A$
7	$\frac{1}{2} - \frac{1}{2}$	$\beta \left\{ \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha) \right\}$	$E_A$
8	$\frac{3}{2} - \frac{1}{2}$	$\beta\beta\beta$	$E_A + 2E_X$

Assuming  $E_A$  to be smaller than  $2E_X$ , the relative order of energies are as follows:

$$(E_A + 2E_X) > E_A > (-E_A + 2E_X) > (E_A - 2E_X) > -E_A > (-E_A - 2E_X)$$

Figure A.3a displays the energy diagram for  $AX_2$  molecule in the absence of spin-spin interactions. Following the selection rule, four A-transitions of equal energy  $2E_A$  and four X-transitions of equal energy  $2E_X$  are observed (Table A.5). Quantum mechanically it can be shown that the probability of each of X-transition is twice as large as that of A-transition. Thus, the intensity of the single line of X-transitions is twice as large as that of the single line of A-transitions.

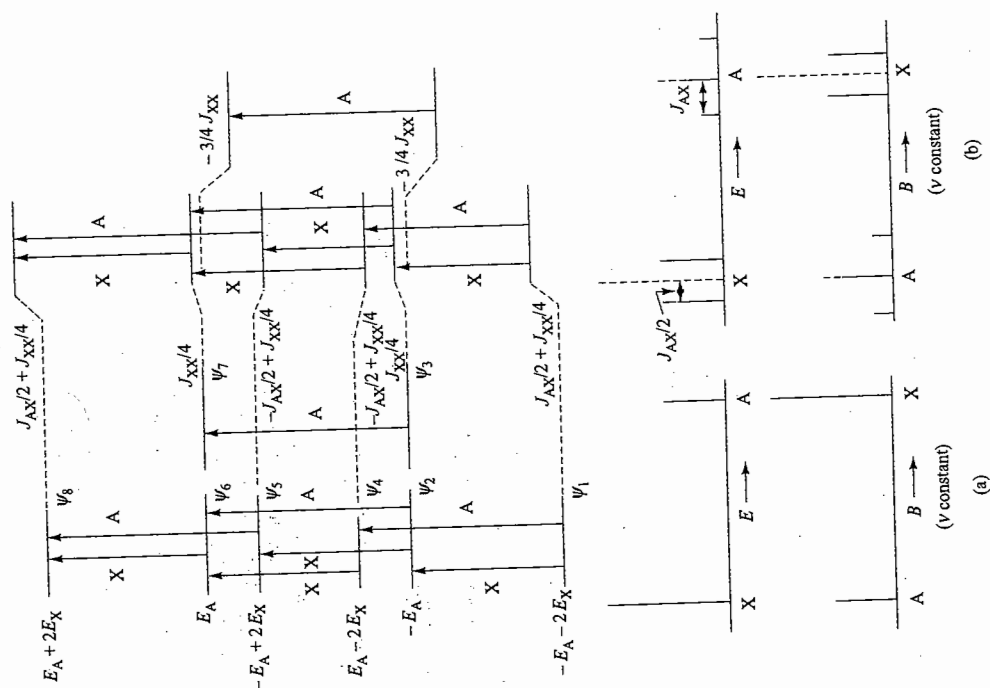


Fig. A.3 Energies of wave functions and allowed spin transitions for the system  $AX_2$ , (a) in the absence of spin-spin interactions, and (b) in the presence of spin-spin interactions

**Table A.5** Allowed Spin Transitions in  $AX_2$  System

Proton undergoing transition	Transition	Energy change
A	$\psi_4 \leftarrow \psi_1$	$2E_A$
A	$\psi_6 \leftarrow \psi_2$	$2E_A$
A	$\psi_8 \leftarrow \psi_3$	$2E_A$
A	$\psi_7 \leftarrow \psi_5$	$2E_A$
X	$\psi_2 \leftarrow \psi_1$	$2E_X$
X	$\psi_5 \leftarrow \psi_4$	$2E_X$
X	$\psi_6 \leftarrow \psi_3$	$2E_X$
X	$\psi_8 \leftarrow \psi_7$	$2E_X$

The energy modification in the presence of spin-spin interactions can be worked out following the principles given below.

1. *Interactions for chemically nonequivalent protons* A pair of parallel spins will repel each other (hence energy increases by an amount  $J_{AX} m_A m_X = J_{AX}/4$ ) whereas that of opposite spins attract each other (hence energy decreases by an amount  $J_{AX}/4$ ).

2. *Interactions for chemically equivalent protons* The interaction between the two protons causes an increase in energy of  $J_{XX}/4$  for a symmetric wave function and a decrease of  $3J_{XX}/4$  for an antisymmetric wave function. As mentioned earlier, these changes do not affect the overall spectrum.

Table A.6 gives the types of interactions and the corresponding energy changes for the eight magnetic states described in Table A.4.

Figure A.3b depicts the above energy changes. Table A.7 gives the energies of the allowed transitions in the presence of spin-spin interactions.

**Table A.6** Energies of Wave Functions in the Presence of Spin-Spin Interactions

State	Types of interactions	Energy
1	$2(\alpha(A)\alpha(X)) + \alpha(X)\alpha(X)$	$-E_A - 2E_X + J_{AX}/2 + J_{XX}/4$
2	$\alpha(A)\alpha(X) + \alpha(A)\beta(X)$ + symmetric $X_2$ wave function	$-E_A + J_{XX}/4$
3	$\alpha(A)\alpha(X) + \alpha(A)\beta(X)$ + antisymmetric $X_2$ wave function	$-E_A - 3J_{XX}/4$
4	$2(\beta(A)\alpha(X))$ + symmetric $X_2$ wave function	$E_A - 2E_X - J_{AX}/2 + J_{XX}/4$
5	$2(\alpha(A)\beta(X))$ + symmetric $X_2$ wave function	$-E_A + 2E_X - J_{AX}/2 + J_{XX}/4$
6	$\beta(A)\alpha(X) + \beta(A)\beta(X)$ + symmetric $X_2$ wave function	$E_A + J_{XX}/4$
7	$\beta(A)\alpha(X) + \beta(A)\beta(X)$ + antisymmetric $X_2$ wave function	$E_A - 3J_{XX}/4$
8	$2(\beta(A)\beta(X))$ + symmetric $X_2$ wave function	$E_A + 2E_X + J_{AX}/2 + J_{XX}/4$

**Table A.7** Spin Transitions for System  $AX_2$  in the Presence of Spin-Spin Interactions

Proton undergoing transition	Transition	Energy change
A	$\psi_4 \leftarrow \psi_1$	$2E_A - J_{AX}$
A	$\psi_6 \leftarrow \psi_2$	$2E_A$
A	$\psi_8 \leftarrow \psi_3$	$2E_A + J_{AX}$
A	$\psi_7 \leftarrow \psi_5$	$2E_A$
X	$\psi_2 \leftarrow \psi_1$	$2E_X - J_{AX}/2$
X	$\psi_5 \leftarrow \psi_4$	$2E_X - J_{AX}/2$
X	$\psi_6 \leftarrow \psi_3$	$2E_X + J_{AX}/2$
X	$\psi_8 \leftarrow \psi_7$	$2E_X + J_{AX}/2$

From Table A.7, we conclude that (i) two of the X transitions have the energy  $2E_X + J_{AX}/2$  while the other two have the energy  $2E_X - J_{AX}/2$ , and (ii) one A transition has the energy  $2E_A + J_{AX}$ , two have the energy  $2E_A$  and one has the energy  $2E_A - J_{AX}$ . Thus, the single transition for the proton X observed in the absence of spin-spin interactions splits into two transitions whereas the single transition of A proton splits into three transitions (Fig. A.3b). The intensities of X-transitions are equal while that of A-transition at  $2E_A$  is twice as intense as the other two transitions.

# 5 Molecular Symmetry and Its Applications

## 5.1 SYMMETRY ELEMENTS AND ASSOCIATED SYMMETRY OPERATIONS

### Introduction

The study of symmetry of a molecule is often useful in making its theoretical and experimental treatments simpler. A point in the molecule is chosen and the symmetry with respect to lines and planes passing through this point is studied. Before studying these in detail, it is worthwhile to make distinction between the symmetry element and the associated symmetry operation.

The symmetry element is a geometrical entity such as a line, a plane or a point with respect to which the symmetry operation is carried out. The associated symmetry operation is actually carrying out the operation on the object. If on carrying out some operation (rotation, reflection, etc.), the object is thrown into a new configuration which is completely indistinguishable from the previous one, the object is said to possess the above symmetry operation and the corresponding symmetry element.

Four types of symmetry elements are used to describe the symmetry of a molecule. A brief description of these symmetry elements and the corresponding symmetry operations is in order.

### Rotations: Axes of Symmetry

An axis of symmetry is a line around which the rotation operation is carried out. The order of rotation axis (symbol:  $n$ ) decides the minimum angle (which is equal to  $360^\circ/n$ ) through which the molecule is rotated clockwise about the axis of symmetry so as to give a new configuration which is indistinguishable from the starting configuration. As per Schönflies notation, the rotation axis is represented by the symbol  $C_n$ .

**$C_2$  Axis of Rotation** An example of a molecule possessing the  $C_2$  axis of rotation is water. The symmetry operation corresponding to this axis of rotation is the rotation by an angle  $180^\circ (= 360^\circ/2)$ . If we label two hydrogen atoms as  $H_a$  and  $H_b$ , the effect of rotating water molecule clockwise by an angle  $180^\circ$  about the axis of rotation (shown by the dotted line) is shown in Fig. 5.1.1.

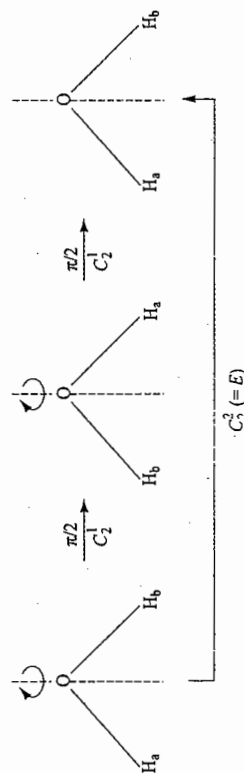


Fig. 5.1.1 The operations  $C_2$  and  $C_2^2$  on water molecule

If we continue rotation by another  $180^\circ$ , we get a configuration which is completely identical to the starting configuration. This consecutive second rotation is represented as  $C_2^2$  (the subscript 2 represents order of axis of rotation and the superscript 2 represents the number of times the rotation operation is carried out)<sup>†</sup>. Since the operation  $C_2^2$  results into a configuration which is completely identical with the starting configuration, this operation is called the *identity operation* (symbol:  $E$ ). Thus, the sequence of operations for a  $C_2$  axis of rotation are  $C_2$  and  $C_2^2 (= E)$ .

### Problem 5.1.1

How many twofold axes of rotation is present in ethylene? Depict these axes of rotation.

### Solution

A molecule of ethylene has three twofold axes of rotation. These are depicted in Fig. 5.1.2.

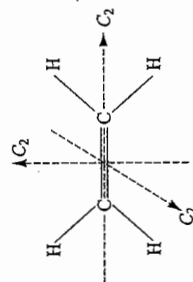


Fig. 5.1.2 Three  $C_2$  axes in ethylene molecule

(i) One  $C_2$  axis is collinear with the C—C axis.

(ii) Second  $C_2$  axis is perpendicular to the plane of the molecule and bisects the C—C line.

(iii) Third  $C_2$  axis is in the plane of the molecule and bisects the C—C line.

**$C_3$  Axis of Rotation** An example of a molecule possessing the  $C_3$  axis of rotation is boron trifluoride. The symmetry operation corresponding to this axis of rotation is the rotation by an angle  $120^\circ (= 360^\circ/3)$ .

Representing the three fluorine atoms as  $F_a$ ,  $F_b$  and  $F_c$ , respectively, the configurations of the molecule after the three successive clockwise rotations of the molecule by an angle  $120^\circ (= 360^\circ/3)$  are shown in Fig. 5.1.3. These three successive rotations are represented as  $C_3$ ,  $C_3^2$  and  $C_3^3$ , respectively. Note that the operations  $C_3$  and  $C_3^2$  produce indistinguishable configurations (II and III) while

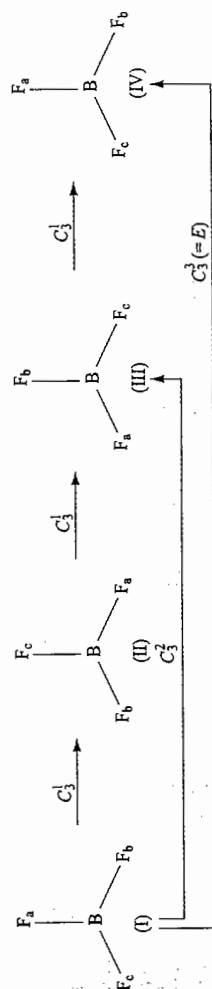


Fig. 5.1.3 The three  $C_3$  operations in succession on boron trifluoride

<sup>†</sup> In general, the notation  $C_n^m$  represents  $n$ -fold axis of rotation and the angle through which the molecule is rotated clockwise is given by  $m \times 2\pi/n$ .

### Simultaneous Existence of $C_2$ and $C_3$ Axes

$C_3$  produces identical configuration (IV) to the starting configuration (I). The operation  $C_3^3$  is also the identity operation. Thus, the sequence of operations for a  $C_3$  axis are  $C_3^1$ ,  $C_3^2$  and  $C_3^3 (= E)$ .

Boron trifluoride also contains three twofold axis of rotation, each passing through one of the F atoms and B atom (Fig. 5.1.4). These axes are perpendicular to the threefold axis of rotation. The existence of two more  $C_2$  axes perpendicular to the  $C_3$  axis implies the presence of two more  $C_2$  axes at angles  $2\pi/3$  and  $4\pi/3$  to generate the first  $C_2$  axis, since the rotations of molecule by  $2\pi/3$  and  $4\pi/3$  about the  $C_3$  axis generate the second and third axes from the first  $C_2$  axis, respectively (Fig. 5.1.4). The three  $C_2$  axes are said to constitute a set of equivalent symmetry elements.

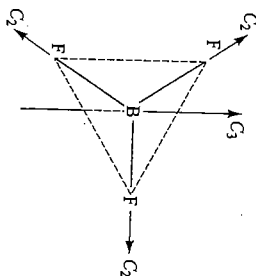


Fig. 5.1.4 Three  $C_2$  axes perpendicular to the  $C_3$  axis in boron trifluoride

### Problem 5.1.2 Solution

Depict the axes of rotations in  $CH_4$  molecule?  
Methane has a regular tetrahedron configuration. It can be depicted within a cube as shown in Fig. 5.1.5.

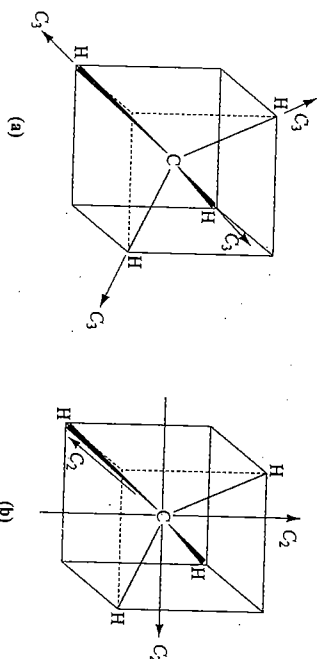


Fig. 5.1.5 A tetrahedron drawn within a cube and depiction of (a)  $C_3$  axes and (b)  $C_2$  axes in methane

Methane has four threefold rotation axes, each passing through one of the hydrogen atoms and carbon atom. These four axes coincide with the C—H bonds (Fig. 5.2.5a). Methane has three twofold rotation axes, each bisecting the bond angles between the two pairs of bonds pointing opposite to each other. These axes also pass through the centre of two opposite faces of the cube in which tetrahedron structure of methane is drawn (Fig. 5.1.5b).

A symmetry plane is a plane through which the operation of reflection is carried out. If atoms in a molecule on reflecting through a plane produces indistinguishable

configuration, the molecule is said to possess a symmetry plane.<sup>†</sup> Obviously, such a plane must pass through the skeleton of the molecule.

**Example** An example of a molecule having a symmetry plane is water, which in fact, contains two symmetry planes: a molecular plane and a plane bisecting HOH bond angle (Fig. 5.1.6).

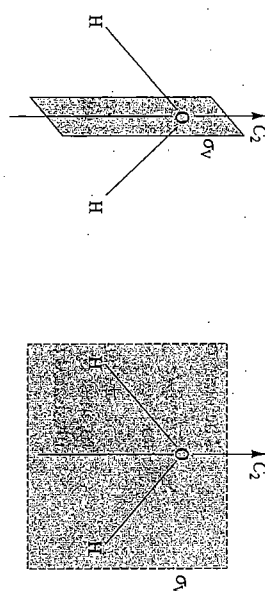


Fig. 5.1.6 Reflection planes in water molecule

Obviously, the two reflection operations carried out in succession produces identity operation, i.e.  $\sigma^2 = E$ . A symmetry plane and the operation of reflection in that plane are represented by the symbol  $\sigma$ . This is further subscripted by the symbols  $v$ ,  $d$  and  $h$ , which respectively stand for vertical, diagonal and horizontal.

**$\sigma_v$  Plane** If the symmetry plane contains the highest-order axis of rotation (known as the principal axis) of a molecule (which is drawn so as to have this axis in a vertical direction), then the plane is known as  $\sigma_v$ . If there are more than one such planes, they are labelled as  $\sigma_v$ ,  $\sigma_v'$ ,  $\sigma_v''$  or  $\{\sigma_v(1), \sigma_v(2), \sigma_v(3)\}$  and so on.

**$\sigma_h$  Plane** If the symmetry plane is perpendicular to the principal axis, it is labelled as  $\sigma_h$ .

**$\sigma_d$  Plane** If the symmetry plane bisects the two  $\sigma_v$  planes, it is labelled as  $\sigma_d$ . These planes are illustrated in Fig. 5.1.7.

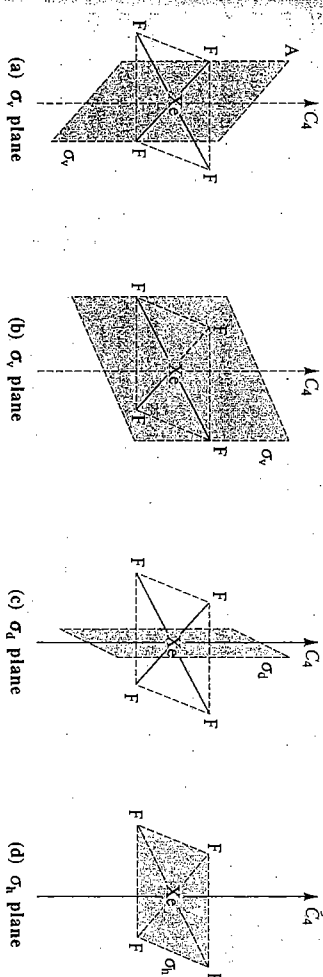


Fig. 5.1.7 Reflection planes in  $XeF_4$

<sup>†</sup> If the molecule contains a single atom of one type, it must lie on the reflection plane. All other atoms lying outside the plane must occur twice in number.

### Reflections: Symmetry Planes



### Inversion: Centre of Symmetry or Centre of Inversion

In the operation of centre of symmetry, a point in the molecule is chosen as the origin of coordinates and each atom of the molecule is shifted to a point whose coordinates are negative of those of the original point. If the obtained configuration is indistinguishable from the original configuration, the molecule is said to possess a centre of symmetry (or centre of inversion) at the origin of coordinates.

The symbol for the centre of inversion and for the corresponding operation is  $i$ . The operation  $i^n = i$  if  $n$  is odd and  $i^n = E$  if  $n$  is even.

**Examples** Examples of molecules having centre of symmetry are  $\text{XeF}_4$ , benzene and acetylene.

The operation of inversion can be regarded as composite movement comprising rotation by  $180^\circ$  followed by reflection in a plane perpendicular to this axis. This is illustrated in Fig. 5.1.8.

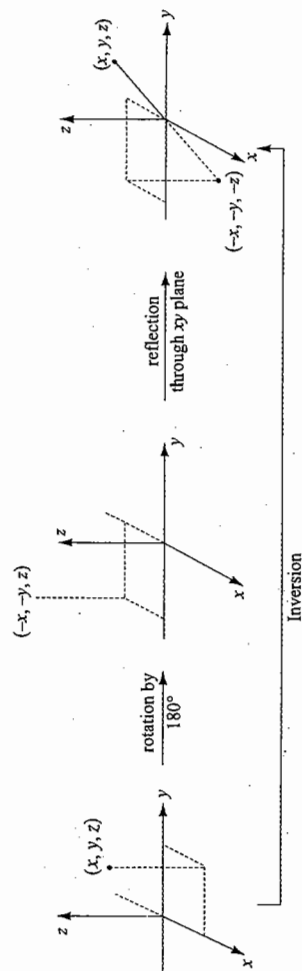


Fig. 5.1.8 Equivalence between inversion operation and the composite operation involving rotation by  $180^\circ$  followed by reflection

### Improper Rotation: Rotation-Reflection Axes

The operation corresponding to the improper rotation axis is  $S_n$ , where  $n$  decides the angle  $2\pi/n$  through which molecule is rotated. The successive improper-rotation operation (rotation followed by reflection) is represented as  $S_n^m$ . It can be shown that the rotation followed by reflection or reflection followed by rotation produces the same result. Thus, the definition of improper rotation need not specify the order.

The symbol of improper rotation axis is  $S_n$ , where  $n$  decides the angle  $2\pi/n$  through which molecule is rotated. The successive improper-rotation operation (rotation followed by reflection) is represented as  $S_n^m$ . It can be shown that the rotation followed by reflection or reflection followed by rotation produces the same result. Thus, the definition of improper rotation need not specify the order.

**Examples** Examples of improper rotation axis are shown by methane (Fig. 5.1.9) and staggered ethane (Fig. 5.1.10).

The sequence of operation shown by the improper axis of rotation of order  $n$  depends whether  $n$  is even or odd. These can be worked out keeping in mind that the order of operations (rotation followed by reflection or reflection followed by rotation) is immaterial (Fig. 5.1.9).

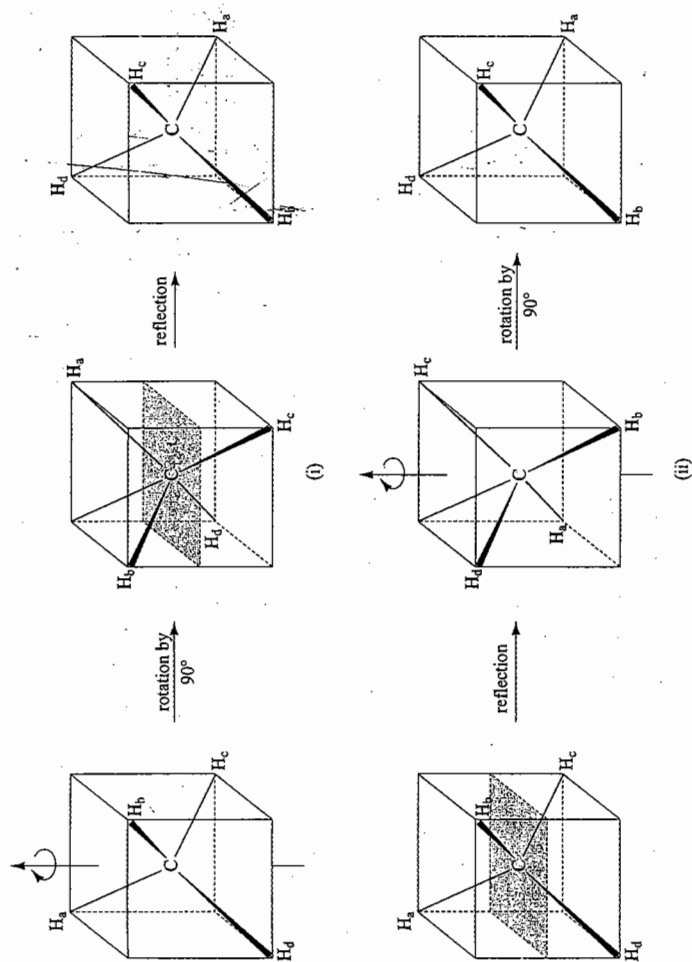


Fig. 5.1.9 The operation  $S_4$  (i) rotation followed by reflection, and (ii) reflection followed by rotation

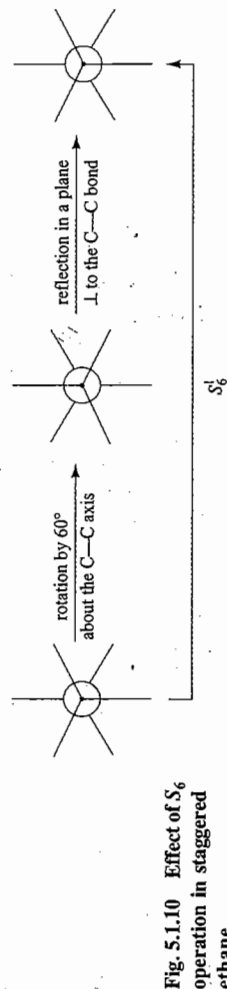


Fig. 5.1.10 Effect of  $S_6$  operation in staggered ethane

### Sequence of Operations for Even Value of $n$

The sequence of operations for  $n = 6$  is as follows.

$$S_6 = \sigma_h C_6 = S_6$$

$$S_6^2 = (\sigma_h C_6)(\sigma_h C_6) = (\sigma_h \sigma_h)(C_6 C_6) = (E)(C_6^2) = C_6^2 = C_6^2$$

$$S_6^3 = (\sigma_h C_6)(\sigma_h C_6)(\sigma_h C_6) = (\sigma_h \sigma_h \sigma_h)(C_6 C_6 C_6) = (\sigma_h)(C_6^3) = (\sigma_h)(C_2) = i$$

$$S_6^4 = (\sigma_h C_6)(\sigma_h C_6)(\sigma_h C_6)(\sigma_h C_6) = (\sigma_h^4)(C_6^4) = (E)(C_6^4) = C_6^4 = C_6^2$$

$$S_6^5 = (\sigma_h C_6)(\sigma_h C_6)(\sigma_h C_6)(\sigma_h C_6)(\sigma_h C_6) = (\sigma_h^5)(C_6^5) = (\sigma_h)(C_6^5) = S_6^5$$

$$S_6^6 = (\sigma_h C_6)(\sigma_h C_6)(\sigma_h C_6)(\sigma_h C_6)(\sigma_h C_6)(\sigma_h C_6) = (\sigma_h^6)(C_6^6) = (E)(E) = E$$

Thus, sequence of operations generated by the element  $S_6$  are  $S_6, C_3, i, C_6^2, S_6^5$  and  $E$ . This set contains  $C_3, C_3^2$ , and  $E$ , which are the operations generated by a

$C_3$  axis. Hence, the existence of the  $S_6$  axis automatically implies the existence of the  $C_3$  axis. Generalization of this statement requires the existence of  $C_{n/2}$  axis if there exists an improper rotation axis of even order.

The repetition of sequence occurs from  $S_n^{n+1}$  onwards.

The sequence of operations for  $n = 5$  is as follows.

$$S_5 = \sigma_h C_5 = S_5$$

$$S_5^2 = (\sigma_h C_5)(\sigma_h C_5) \equiv (\sigma_h \sigma_h) (C_5 C_5) \equiv (E)(C_5^2) \equiv C_5^2$$

$$S_5^3 = (\sigma_h C_5)(\sigma_h C_5)(\sigma_h C_5) \equiv (\sigma_h \sigma_h \sigma_h) (C_5 C_5 C_5) = (\sigma_h)(C_5^3) = S_5^3$$

$$S_5^4 = (\sigma_h C_5)^4 \equiv (\sigma_h^4)(C_5^4) \equiv (E)(C_5^4) = C_5^4$$

$$S_5^5 = (\sigma_h C_5)^5 \equiv (\sigma_h^5)(C_5^5) \equiv (\sigma_h)(E) = \sigma_h$$

$$S_5^6 = (\sigma_h C_5)^6 \equiv (\sigma_h^6)(C_5^6) \equiv (E)(C_5^1) = C_5^1$$

$$S_5^7 \equiv (\sigma_h C_5)^7 \equiv (\sigma_h^7)(C_5^7) \equiv (\sigma_h)(C_5^2) = S_5^2$$

$$S_5^8 \equiv (\sigma_h C_5)^8 \equiv (\sigma_h^8)(C_5^8) \equiv (E)(C_5^3) = C_5^3$$

$$S_5^9 \equiv (\sigma_h C_5)^9 \equiv (\sigma_h^9)(C_5^9) \equiv (\sigma_h)(C_5^4) = S_5^4$$

$$S_5^{10} \equiv (\sigma_h C_5)^{10} \equiv (\sigma_h^{10})(C_5^{10}) \equiv (E)(C_5^5) \equiv (E)(E) \equiv (E)$$

The sequence of operations generated by  $S_n$  with  $n$  odd are  $2n$  in numbers. For  $S_5$ , these are  $S_5^1, C_5^2, S_5^3, C_5^4, \sigma_h, C_5^1, S_5^2, C_5^3, S_5^4$ , and  $E$ . The repetition of sequence occurs from  $S_n^{2n+1}$  onwards.

It may be noted that an  $S_1$  operation is equivalent to a reflection operation and an  $S_2$  operation is equivalent to an inversion operation.

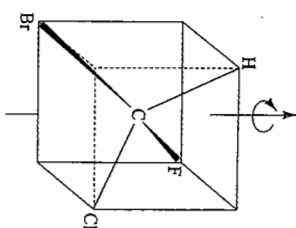
A molecule having no improper rotation axis is dissymmetric. This implies that such a molecule is not superimposable on its mirror image and thus shows optical isomerism.

## 5.2 CLASSIFICATION OF MOLECULES BASED ON SYMMETRY ELEMENTS

A molecule may be classified into different categories (known as *point groups*) based on its symmetry elements. We start with the minimum symmetry element of identity (or rotation by  $360^\circ$ ) and continue adding more and more symmetry elements one by one. The Schönflies symbols ( $C_n, \sigma, i$  and  $S_n$ ) are used to represent different point groups.

**Point Group  $C_1$**  This group includes molecules having only identity element or  $C_1$  axis of rotation. An example of this group is a carbon atom attached to four different atoms, e.g.  $\text{CHFClBr}$  (Fig. 5.2.1).

Fig. 5.2.1 An example of the point group  $C_1$



Point Group  $C_n$

This group includes molecules having only one axis of symmetry of order  $n$  (more than one). The sequence of operations associated with the group  $C_n$  is  $C_n^1, C_n^2, \dots, C_n^{n-1}, C_n^n (= E)$ . Very few molecules belong to this point group.

This group includes molecules having only one symmetry plane. The sequence of operations associated with the  $C_s$  group is  $\sigma$  and  $\sigma^2 (= E)$ . An example of this group is  $\text{SO}_2, \text{BrF}$  (Fig. 5.2.2).

Point Group  $C_s$

This group includes molecules having only a centre of symmetry. The sequence of operations associated with this group is  $i$  and  $i^2 (= E)$ . An example of this group is staggered  $\text{CHClBr}-\text{CHClBr}$  (Fig. 5.2.3).

Fig. 5.2.2 An example of the point group  $C_s$

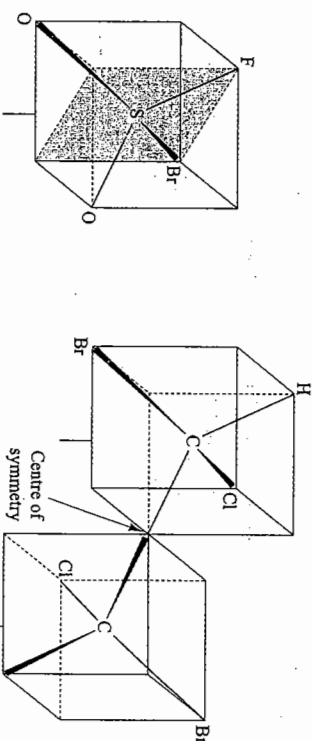


Fig. 5.2.3 An example of the point group  $C_i$

Point Group  $C_{nv}$

This group includes molecules having an axis of symmetry,  $C_n$ , along with  $n$  vertical planes. The sequence of operations associated with the group  $C_{nv}$  are  $C_n, C_n^2, C_n^3, \dots, C_n^n, \sigma_v, \sigma_v', \dots$  (a total  $n$  planes). Examples of this group are described in the following.

**Point group  $C_{2v}$**  Example is water (Fig. 5.2.4). The elements are  $C_2, \sigma_v$  and  $\sigma_v'$ . The operations are  $C_2, C_2^2 (= E), \sigma_v$  and  $\sigma_v'$ .

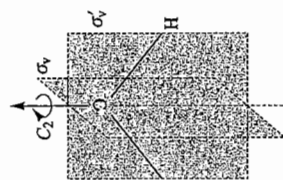


Fig. 5.2.4 An example of the point group  $C_{3v}$

**Point group  $C_{3v}$**  Examples are  $\text{NH}_3$  and  $\text{PCl}_3$ . The operations are  $C_3$ ,  $C_3^2$ ,  $C_3^3 (= E)$ ,  $\sigma_v$ ,  $\sigma_v'$  and  $\sigma_v''$ . The axis  $C_3$  passes through N atom and centre of equilateral triangle formed by the three H atoms. The reflection plane  $\sigma_v$  includes N atom and one of the H atoms and passes through the centre of the other two H atoms. Since there are three H atoms, there will be three reflection planes (Fig. 5.2.5).

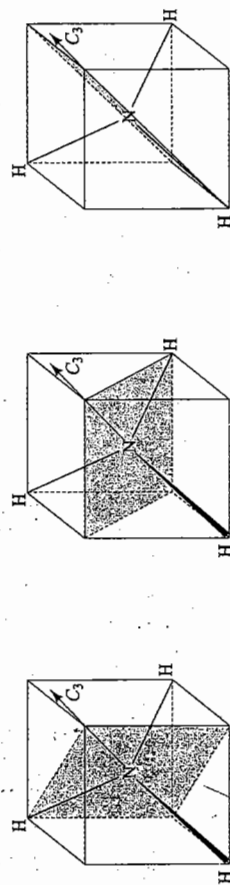


Fig. 5.2.5  $C_3$  axis and three vertical planes in  $\text{NH}_3$  molecule

**Point group  $C_{4v}$**  Example is  $\text{BrF}_5$  (Fig. 5.2.6). The  $C_4$  axis passes through the apex F and the central Br atoms. There are four  $\sigma_v$  symmetrical planes (in fact, two are labelled as  $\sigma_v$  and two are labelled as  $\sigma_d$ ).

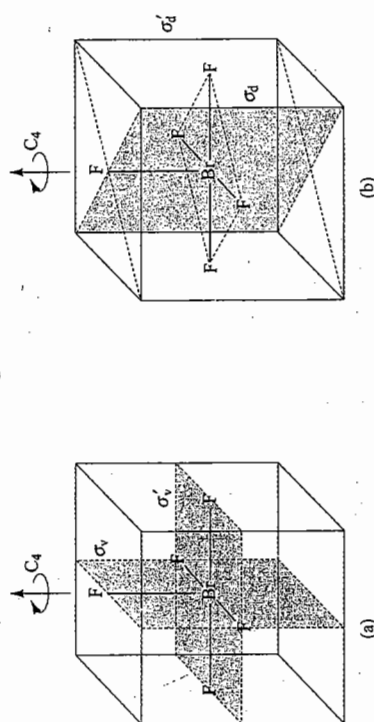
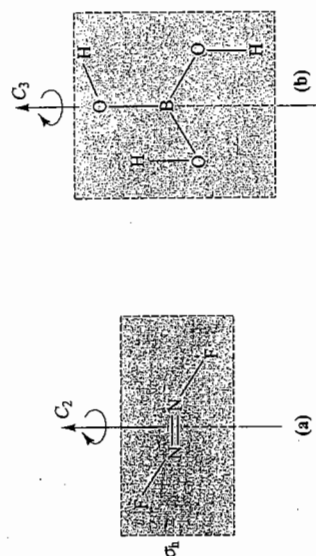


Fig. 5.2.6 An example of the point group  $C_{4v}$

This point group includes molecules having an axis of symmetry,  $C_n$ , along with one horizontal plane of symmetry. Examples of this group are  $\text{trans-N}_2\text{F}_2$  and  $\text{H}_3\text{BO}_3$  (Fig. 5.2.7).

**Point Group  $C_{nh}$**

Fig. 5.2.7 Examples of (a)  $C_{2h}$  and (b)  $C_{3h}$  groups



**Point Group  $S_{2n}$**

This point group includes molecules having an  $S_{2n}$  axis coincident with a  $C_{2n}$  axis. The group  $S_2$  is the same as the group  $C_i$ , as a rotation by  $180^\circ$  followed by reflection in the horizontal plane is equivalent to an inversion  $i$ .

**Point Group  $D_n$**

This point group includes molecules having a  $C_n$  axis along with  $n$  twofold axes right angles to the  $C_n$  axis. Example of  $D_3$  group is the gauche conformation of ethane.

**Point Group  $D_{nh}$**

This point group includes molecules having an axis of symmetry,  $C_n$ , along with  $n$  twofold axes right angle to the  $C_n$  axis and a horizontal symmetrical plane. Examples of this group are as follows.

$D_{2h}$   $\text{CH}_2=\text{CH}_2$ ;  $C_2$  axis, two twofold axes perpendicular to the  $C_2$  axis and  $\sigma_h$  plane.

$D_{3h}$   $\text{CO}_3^{2-}$ ;  $C_3$  axis, three twofold axes perpendicular to the  $C_3$  axis and  $\sigma_h$  plane.

$D_{4h}$   $\text{XeF}_4$ ;  $C_4$  axis, four twofold axes perpendicular to the  $C_4$  axis and  $\sigma_h$  plane.

$D_{6h}$   $\text{C}_6\text{H}_6$ ;  $C_6$  axis, six twofold axes perpendicular to the  $C_6$  axis and  $\sigma_h$  plane.

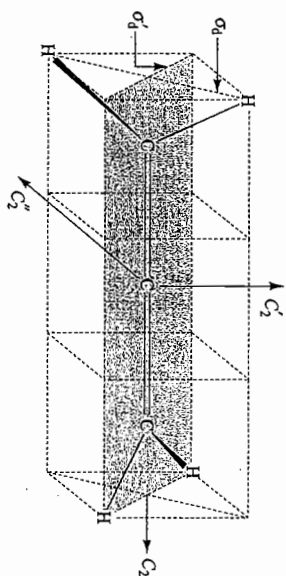
**Point Group  $D_{nd}$**

This point group includes molecules having a  $C_n$  axis of symmetry along with  $n$  twofold axes of symmetry perpendicular to the  $C_n$  axis and  $n$  vertical symmetry planes bisecting the angles between  $C_2'$  axes (these planes are known as dihedral planes of symmetry,  $\sigma_d$ ). An example of the group  $D_{2d}$  is allene ( $\text{C}_3\text{H}_4$ ), shown in Fig. 5.2.8. This molecule possesses  $C_2$  axis, two twofold axes perpendicular to the  $C_2$  axis and two  $\sigma_d$  planes.

**Point Group  $C_{\infty v}$**

The point group  $C_{\infty v}$  includes linear molecules without a centre of symmetry. Examples include  $\text{H}-\text{Cl}$  and  $\text{O}=\text{C}=\text{S}$ . These molecules contain a  $C_\infty$  axis of rotation coinciding with internuclear axis along with an infinite number of  $\sigma_v$  planes.

Fig. 5.2.8 An example of the point group  $D_{\infty h}$



### Point Group $D_{\infty h}$

The point group  $D_{\infty h}$  includes linear molecules with a centre of symmetry. Examples include homonuclear diatomic molecules and  $H-C\equiv C-H$ . These molecules contain a  $C_{\infty}$  axis of rotation coinciding with internuclear axis, a  $C_2$  plane and an infinite number of  $C_2'$  axes perpendicular to the  $C_{\infty}$  axis.

### Point Group $T_d$

The point group  $T_d$  includes symmetry elements possessed by a tetrahedron. These are easily visualised by drawing a tetrahedron within a cube (Fig. 5.2.9).

A tetrahedron has the following symmetry elements.

- Four  $C_3$  axes of rotation; each passing through two opposite apices of the cube (i.e. one apex and the centre of the opposite face of the tetrahedron). Each of these axes generates  $C_3$  and  $C_3^2$  operations—a total of eight operations.
- Three  $S_4$  axes of rotation; each passing through the centres of an opposite pairs of faces of the cube. Each of these generates the operations  $S_4$ ,  $S_4^2$  ( $= C_2$ ), and  $S_4^3$ —a total of six operations excluding the operations  $C_2$ .
- Three  $C_2$  axes of rotation; each passing through the centres of an opposite pairs of faces of the cube. Each of these axes generates an operation  $C_2$  which are already included in  $S_4$  operations.
- Six  $\sigma_d$  planes of symmetry; each passing through two vertices and bisecting the line joining the other two vertices of the cube. These generate six operations  $\sigma_d$ .

Thus, we have the following set of symmetry operations in the point group  $T_d$ .

$$E, 8C_3, 3C_2, 6S_4, 6\sigma_d$$

These are 24 in number.

The point group  $O_h$  includes symmetry elements possessed by an octahedron. These are easily visualised by drawing an octahedron within a cube (Fig. 5.2.10).

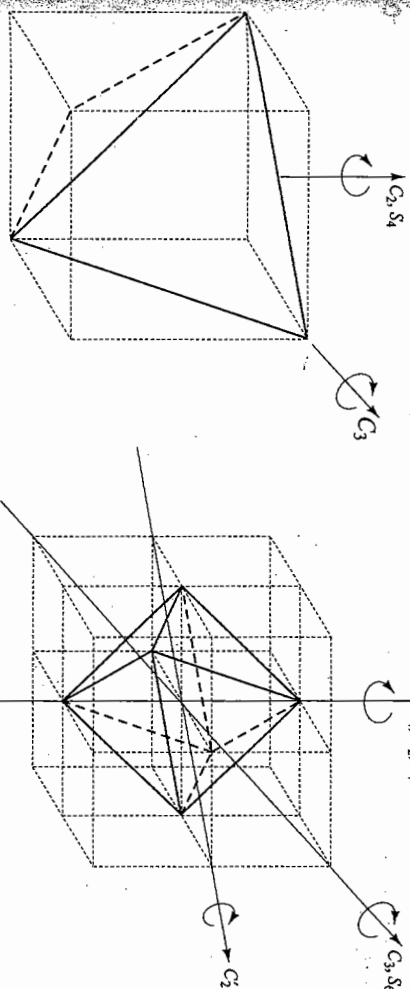


Fig. 5.2.9 A tetrahedron drawn within a cube

Fig. 5.2.10 An octahedron drawn within a cube

An octahedron has the following symmetry elements.

- Three  $S_4$  axes of rotation; each passing through opposite apices. Each generates the operations  $S_4$ ,  $S_4^2$  ( $= C_2$ ) and  $S_4^3$ —a total of six operations excluding the operations  $C_2$ .
- Three  $C_2$  axes of rotation coinciding with the  $S_4$  axes, respectively. Each of these generates the operation  $C_2$  which are already included in the  $S_4$  operations.
- Three  $C_4$  axes of rotation coinciding with the  $S_4$ s and  $C_2$ s axes. Each of these generates the operations  $C_4$ ,  $C_4^2$  ( $= 2C_2$ ) and  $C_4^3$ . These generate six operations excluding the operations  $C_2$ s.
- Four  $S_6$  axes of rotation; each passing through the centres of a pair of opposite triangular faces. Each of these generates the operations  $S_6$ ,  $S_6^2$  ( $= C_3$ ),  $S_6^3$  ( $= i$ ),  $S_6^4$  ( $= C_3^2$ ) and  $S_6^5$ —a total of eight operations excluding  $S_6^2$ ,  $S_6^3$  and  $S_6^4$ .
- Six  $C_2'$  axes; each passing through the centre of opposite edges. These generate six  $C_2$  operations.
- Four  $C_3$  axes coinciding with the  $S_6$ s. Each generates  $C_3$  and  $C_3^2$  operations which are also generated by the  $S_6$  axes.
- An inversion centre; this generates the operation of inversion. This is also generated by each of the  $S_6$  operations.
- Three horizontal planes  $\sigma_h$ ; each passing through four of the six apices.
- Six vertical planes  $\sigma_v$ ; each passing through two apices and bisecting two opposite edges. Each of these generates an operation  $\sigma_d$ .

Thus, we have the following set of symmetry operations in the point group  $O_h$ .

$$E, 8C_3, 6C_4, 6C_2, 3C_2' (= C_4^2), i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d$$

These are 48 in number.

This is highly symmetrical group with  $h = 120$ . These are  $E$ ,  $12C_3$ ,  $12C_2$ ,  $20C_4$ ,  $15C_2'$ ,  $i$ ,  $12S_6$ ,  $12S_4$ ,  $20S_6$  and  $15\sigma$ . Examples include regular icosahedron and dodecahedron and Buckminster fullerene ( $C_{60}$ ).

### Point Group $I_h$

### Systematic Classification of Molecules

A systematic procedure for classifying a molecule in its point group is shown in Fig. 5.2.11. It is self-explanatory.

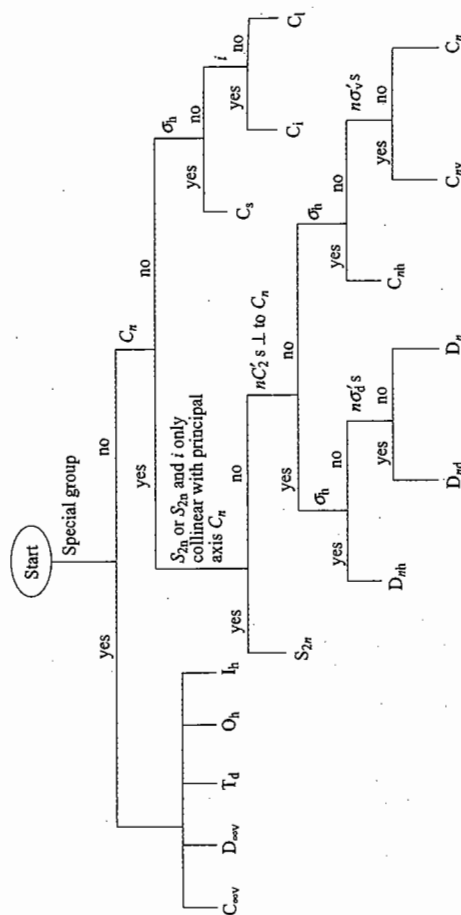


Fig. 5.2.11 A systematic way of classifying a molecule in its point group

### 5.3 MATRIX REPRESENTATIONS OF GEOMETRICAL OPERATIONS

The effect of a geometric operation on a point (or a collection of points) can be expressed mathematically by using the matrix notations.

Let  $P(x, y, z)$  be the position of a point (Fig. 5.3.1). Let this point be shifted to the point  $P'(x', y', z')$  after carrying out one of the symmetry operations listed earlier. The coordinates  $(x', y', z')$  may be correlated with  $(x, y, z)$  in the form of matrix notations.

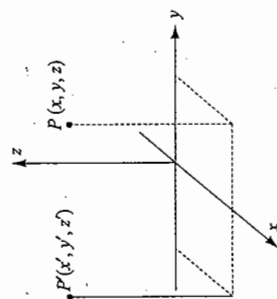


Fig. 5.3.1 Cartesian axes

#### Identity Operation

In an identity operation, the new coordinates  $(x', y', z')$  are the same as the initial ones, i.e.  $(x, y, z)$ . This fact, in the matrix notation, is expressed as

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

The  $3 \times 3$  unit matrix represents the identity operation.

#### Reflection Operation

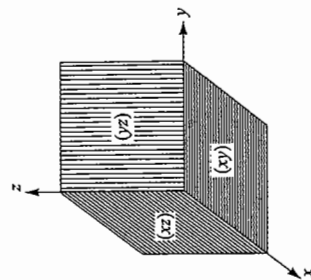


Fig. 5.3.2 Reflection planes

In carrying out the reflection in such planes, only the coordinate perpendicular to the plane changes sign while the other two coordinates remain the same. Hence, we have

$$\sigma_{xy}: \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (x, y, z) \rightarrow (x, y, -z)$$

$$\sigma_{xz}: \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (x, y, z) \rightarrow (x, -y, z)$$

$$\sigma_{yz}: \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (x, y, z) \rightarrow (-x, y, z)$$

In the inverse operation, all the three coordinates of a point change sign, i.e.

$$i: \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (x, y, z) \rightarrow (-x, -y, -z)$$

Let the rotation be carried out clockwise by an angle  $\theta$  about the  $z$ -axis (Fig. 5.3.3). After the rotation, the coordinate  $z$  remains unaffected, i.e.  $z' = z$ . The expressions of  $(x', y')$  in terms of  $(x, y)$  may be derived by considering the rotations of  $x$ -component and  $y$ -component vectors clockwise by an angle  $\theta$ . The  $x$ - and  $y$ -components of the rotated vectors are as follows.

$$x\text{-component vector} \quad x_1 = x \cos \theta \quad \text{and} \quad y_1 = -x \sin \theta$$

$$y\text{-component vector} \quad x_2 = y \sin \theta \quad \text{and} \quad y_2 = y \cos \theta$$

$$\text{Hence,} \quad x' = x_1 + x_2 = x \cos \theta + y \sin \theta$$

$$y' = y_1 + y_2 = -x \sin \theta + y \cos \theta$$

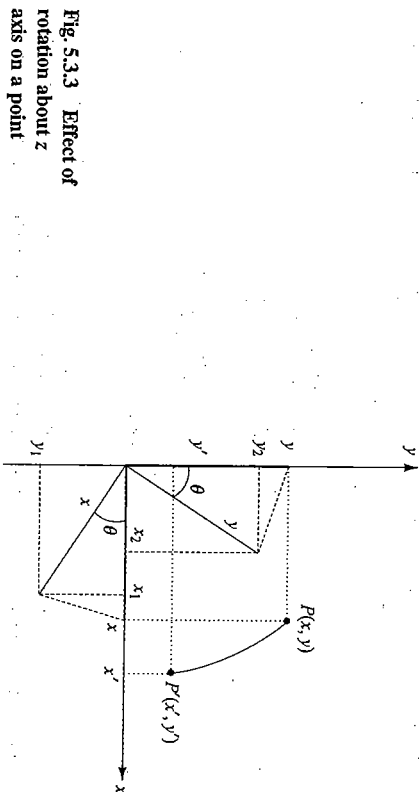


Fig. 5.3.3 Effect of rotation about  $z$  axis on a point

### Alternative Procedure

Let the vector  $OP$  (shown in Fig. 5.3.4a) be thrown into  $OP'$  (shown in Fig. 5.3.4b) when the former is rotated clockwise by an angle  $\theta$  about the  $z$ -axis.

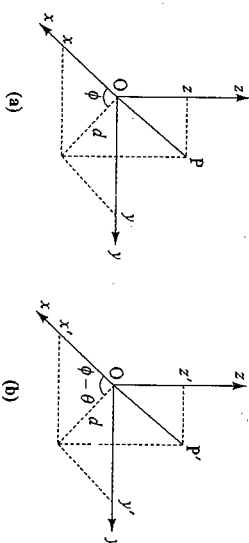


Fig. 5.3.4 Rotation of  $OP$  clockwise by an angle  $\theta$  about the  $z$ -axis

From Fig. 5.3.4a, we have  $x = d \cos \phi$  and  $y = d \sin \phi$

From Fig. 5.3.4b, we have

$$\begin{aligned} x' &= d \cos(\phi - \theta) = d \cos \phi \cos \theta + d \sin \phi \sin \theta \\ &= d(x/d) \cos \theta + d(y/d) \sin \theta = x \cos \theta + y \sin \theta \\ y' &= d \sin(\phi - \theta) = d \sin \phi \cos \theta - d \cos \phi \sin \theta \\ &= d(y/d) \cos \theta - d(x/d) \sin \theta = y \cos \theta - x \sin \theta \end{aligned}$$

In the matrix notation, we have

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

### Improper Rotation Operations

This operation involves rotation about an axis followed by reflection in a plane perpendicular to the axis of rotation. If the rotation is carried out about  $z$ -axis, then the reflection to be considered is in the  $xy$  plane. The latter operation causes the reversal of sign of  $z$  component. Hence,  $z' = -z$ . Thus, the matrix representing improper rotation is obtained from that of proper rotation by changing 1 to  $-1$ . The obtained matrix is

### Utility of Matrix Notation

If an object is subjected to more than one symmetry operation in succession, the net result can be obtained by left multiplying the corresponding matrices in the same order. For example, if we carry out the reflection operations  $\sigma_{yz}$  and  $\sigma_{xz}$  in succession, we will have

$$\begin{aligned} \sigma_{xz} \sigma_{yz} &\equiv \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ &\equiv \begin{pmatrix} \cos 180^\circ & \sin 180^\circ & 0 \\ -\sin 180^\circ & \cos 180^\circ & 0 \\ 0 & 0 & 1 \end{pmatrix} \equiv C_2(z) \end{aligned}$$

that is, the net result is to carry out the clockwise rotation by  $180^\circ$  about the  $z$ -axis [i.e.  $C_2(z)$  operation].

### 5.4 DEFINITION OF A GROUP

In the mathematical sense, a group is a collection of elements satisfying the following four characteristics.

#### Combination of Elements

Any combination of two or more elements of the collection must be equivalent to one element which is also a member of the collection.

The combination of two elements, say  $A$  and  $B$ , is written either as  $AB$  (spelled as  $B$  left-multiplied by  $A$ ) or  $BA$  (spelled as  $B$  right-multiplied by  $A$ ). The result of this combination is one of the elements of the same group.

The combination is said to be *commutative* if  $AB = BA$ , i.e. the result is the same. A group satisfying this condition is said to be *Abelian group*.

The combination is said to be *noncommutative* if  $AB \neq BA$ , i.e. the order in which the combination is carried out yields different elements of the same group.

One element in the group must commute with all other members and leave them unchanged. This element is called the identity element and is designated by the symbol  $E$ . If  $A$  and  $B$  are other elements, then we have

$$AE = EA = A \quad \text{and} \quad BE = EB = B$$

#### Associative Law of Multiplication

The combination of more than two elements satisfies the associative law of multiplication. This implies that

$$A(BC) = (AB)C$$

that is, the combination  $BC$  when left-multiplied by  $A$  yields the same result as the combination  $AB$  right-multiplied by  $C$ .

### Reciprocal of Elements

Every member of a group has a reciprocal, which is also an element of the group.

By definition, the reciprocal of  $A$  is  $X$  such that  $AX = XA = E$

The reciprocal  $X$  in the above expression is also written as  $A^{-1}$ .

### Problem 5.4.1

Show that the reciprocal of a combination of two (or more) elements of a group is equal to the combination of the reciprocals in the reverse order.

### Solution

Let  $AB = D$

Right multiplication on both sides by  $B^{-1}A^{-1}$ , we get

$$AB B^{-1}A^{-1} = DB^{-1}A^{-1}$$

i.e.

$$A(BB^{-1})A^{-1} = DB^{-1}A^{-1}$$

or

$$AEA^{-1} = DB^{-1}A^{-1} \quad (\text{since } BB^{-1} = E)$$

i.e.

$$(AE)A^{-1} = DB^{-1}A^{-1}$$

or

$$AA^{-1} = DB^{-1}A^{-1} \quad (\text{since } AE = A)$$

or

$$E = DB^{-1}A^{-1}$$

This implies that  $B^{-1}A^{-1}$  is the reciprocal of  $D$ , which by definition, is  $AB$ .

## 5.5 GROUP CONSISTING OF SYMMETRY OPERATIONS ON A MOLECULE

### Point Group Consisting of Symmetry Operations

All symmetry operations of a molecule taken together constitute a group, known as *point group*. It satisfies all the four characteristics of a group. Before demonstrating these characteristics, it is worth considering the group-multiplication table of operations of a point group.

The binary products of symmetry operations of a point group are shown in the form of a group multiplication table. The table includes as many rows and columns as the number of symmetry operations of a molecule. Each row and each column are headed by a symmetry operation. Their product is shown under the given column and along the given row. The order of multiplication is (column element)  $\times$  (row element). This is being illustrated by taking the examples of  $\text{H}_2\text{O}$  (point group  $C_{2v}$ ) and  $\text{NH}_3$  molecules (point group  $C_{3v}$ ).

### Transformation Matrices for the Point Group $C_{2v}$

The symmetry elements in water are  $E$ ,  $C_2$ ,  $\sigma_v$  and  $\sigma'_v$ . The reflection plane  $\sigma_v$  bisects the angle  $\text{HOH}$  and  $\sigma'_v$  coincides with the molecular plane. Since water molecule is a planar molecule, the geometric operations may be described by  $2 \times 2$  matrices. These matrices can be worked out by the inspection of Fig. 5.5.1.

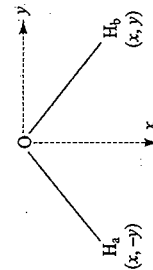


Fig. 5.5.1  
Orientation of  
water molecule

**$E$  operation** The coordinates of a point remain unchanged in the  $E$  operation. Hence,

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

**$C_2$  operation** The rotation about  $x$ -axis by  $180^\circ$  changes the  $y$  component of a point. Hence,

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

**$\sigma_v$  operation** The reflection plane  $\sigma_v$  changes the  $y$  component of a point. Hence

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

**$\sigma'_v$  operation** The reflection plane  $\sigma'_v$  does not change the coordinates of a point. Hence

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

### Group Multiplication Table of the Point Group $C_{2v}$

The group multiplication table of the point group  $C_{2v}$  is shown in Table 5.5.1. The entries shown within squares can be written straight-way as (i) the multiplication of an operation with an identity operation leaves it unchanged, and (ii) the operations  $C_2 C_2 (= E)$ ,  $\sigma_v \sigma_v (= E)$  and  $\sigma'_v \sigma'_v (= E)$  are equivalent to the identity operations.

Table 5.5.1 Group Multiplication Table of the Point Group  $C_{2v}$

$C_{2v}$	$E$	$C_2$	$\sigma_v$	$\sigma'_v$
$E$	$E$	$C_2$	$\sigma_v$	$\sigma'_v$
$C_2$	$C_2$	$E$	$\sigma'_v$	$\sigma_v$
$\sigma_v$	$\sigma_v$	$\sigma'_v$	$E$	$C_2$
$\sigma'_v$	$\sigma'_v$	$\sigma_v$	$C_2$	$E$

The rest of the combinations can be worked out either by carrying out the operations in succession in the order shown (starting from the operation written at the extreme right and proceeding one by one to the left) or by multiplication of the corresponding matrices. The six remaining combinations to be worked out in Table 5.5.1 are as follows.<sup>†</sup>

<sup>†</sup> We include only  $H_a$  and  $H_b$  as their positions get affected in the symmetry operations. The position of oxygen remains unaffected.



- $\sigma_v C_2 [H_a; H_b] \rightarrow \sigma_v [H_b; H_a] \rightarrow [H_a; H_b] \equiv \sigma_v' [H_a; H_b]$  that is,  $\sigma_v C_2 \equiv \sigma_v'$

Using the matrix notations, we have  $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

$$\sigma_v \quad C_2 \quad \sigma_v'$$

- $\sigma_v' C_2 [H_a; H_b] \rightarrow \sigma_v' [H_b; H_a] \rightarrow [H_a; H_b] \equiv \sigma_v [H_a; H_b]$  that is,  $\sigma_v' C_2 = \sigma_v$

Using the matrix notations, we have  $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$$\sigma_v' \quad C_2 \quad \sigma_v$$

- $C_2 \sigma_v [H_a; H_b] \rightarrow C_2 [H_b; H_a] \rightarrow [H_a; H_b] \equiv \sigma_v' [H_a; H_b]$  that is,  $C_2 \sigma_v \equiv \sigma_v'$

Using the matrix notations, we have  $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

$$C_2 \quad \sigma_v \quad \sigma_v'$$

- $C_2 \sigma_v' [H_a; H_b] \rightarrow C_2 [H_b; H_a] \rightarrow [H_a; H_b] \equiv \sigma_v [H_a; H_b]$  that is,  $C_2 \sigma_v' \equiv \sigma_v$

Using the matrix notations, we have  $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$$C_2 \quad \sigma_v' \quad \sigma_v$$

- $\sigma_v \sigma_v' [H_a; H_b] \rightarrow \sigma_v [H_a; H_b] \rightarrow [H_b; H_a] \equiv C_2 [H_a; H_b]$  that is,  $\sigma_v \sigma_v' \equiv C_2$

Using the matrix notations, we have  $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$$\sigma_v \quad \sigma_v' \quad C_2$$

- $\sigma_v' \sigma_v [H_a; H_b] \rightarrow \sigma_v' [H_b; H_a] \rightarrow [H_a; H_b] \equiv C_2 [H_a; H_b]$  that is,  $\sigma_v' \sigma_v \equiv C_2$

Using the matrix notations, we have  $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$$\sigma_v' \quad \sigma_v \quad C_2$$

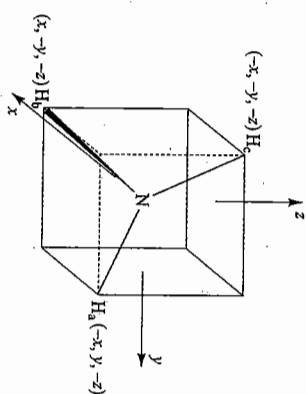
The following points from Table 5.5.1 may be highlighted.

- Each row and each column includes each symmetry operation once and only once.
- Each row and each column is a rearranged list of the symmetry operations.
- No two rows (or two columns) are identical.

### Transformation Matrices for the Point Group $C_{3v}$

The symmetry elements in ammonia are  $E$ ,  $C_3$ ,  $\sigma_v(1)$ ,  $\sigma_v(2)$  and  $\sigma_v(3)$ . The corresponding symmetry operations are  $E$ ,  $C_3$ ,  $C_3^2$ ,  $\sigma_v(1)$ ,  $\sigma_v(2)$  and  $\sigma_v(3)$ . Figure 5.5.2 displays an ammonia molecule along with the Cartesian axes.

Fig. 5.5.2 Ammonia molecule within a cube



The matrices for the operations  $E$ ,  $C_3$ ,  $C_3^2$ ,  $\sigma_v(1)$ ,  $\sigma_v(2)$  and  $\sigma_v(3)$  can be built up as shown in the following.

**Operation  $E$**  The operation  $E$  does not change the coordinate of a point. Hence

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

new coordinates  $E$  old coordinates

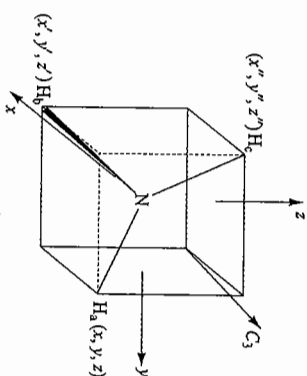
**Operation  $C_3$**  The  $C_3$  axis of rotation is shown in Fig. 5.5.3.

The rotation by  $2\pi/3$  about the  $C_3$  axis throws  $H_a$  to  $H_b$ ,  $H_b$  to  $H_c$  and  $H_c$  to  $H_a$ . This rotation also sends the axis  $x$  into  $z$ ,  $y$  into  $x$  and  $z$  into  $y$ . Thus, the coordinates of a point (say, those of  $H_a$ ) after rotation change according to the following scheme.

$$x' = y, \quad y' = z \quad \text{and} \quad z' = x$$

In matrix notation, this change is expressed as

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$



**Operation  $C_3^2$**  This rotation sends  $H_a$  to  $H_c$ ,  $H_b$  to  $H_a$  and  $H_c$  to  $H_b$ . This rotation also sends the axis  $x$  into  $y$ ,  $y$  into  $z$  and  $z$  into  $x$ . Thus, the coordinates of a point (say, those of  $H_a$ ) after rotation change according to the following scheme.

$$x' = z, \quad y' = x \quad \text{and} \quad z' = y$$



$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

In the matrix notation, this change is expressed as

**Operation  $\sigma_v(1)$**  The reflection plane  $\sigma_v(1)$  is shown in Fig. 5.5.4a.

The reflection through  $\sigma_v(1)$  shifts  $H_a$  to  $H_b$  and  $H_b$  to  $H_a$ . This reflection also sends the axis  $x$  into  $y$  and  $y$  into  $x$ . Thus, the coordinates of a point (say, those of  $H_c$ ) after reflection change according to the following scheme.

$$x' = y, \quad y' = x \quad \text{and} \quad z' = z$$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

In matrix notation, this change is expressed as

**Operation  $\sigma_v(2)$**  The reflection plane  $\sigma_v(2)$  is shown in Fig. 5.5.4b.

The reflection through  $\sigma_v(2)$  shifts  $H_b$  to  $H_c$  and  $H_c$  to  $H_b$ . This reflection also sends the axis  $x$  into  $z$  and  $z$  into  $x$ . Thus, the coordinates of a point (say, those of  $H_a$ ) after reflection change according to scheme given below.

$$x' = z, \quad y' = y \quad \text{and} \quad z' = x$$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

In the matrix notation, this change is expressed as

**Operation  $\sigma_v(3)$**  The reflection plane  $\sigma_v(3)$  is shown in Fig. 5.5.4c.

The reflection through  $\sigma_v(3)$  shifts  $H_a$  into  $H_c$  and  $H_c$  into  $H_a$ . This reflection also sends the axis  $y$  into  $z$  and  $z$  into  $y$ . The coordinates of a point (say, those of  $H_b$ ) after reflection change according to scheme given below.

$$x' = x, \quad y' = z \quad \text{and} \quad z' = y$$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

In the matrix notation, this change is expressed as

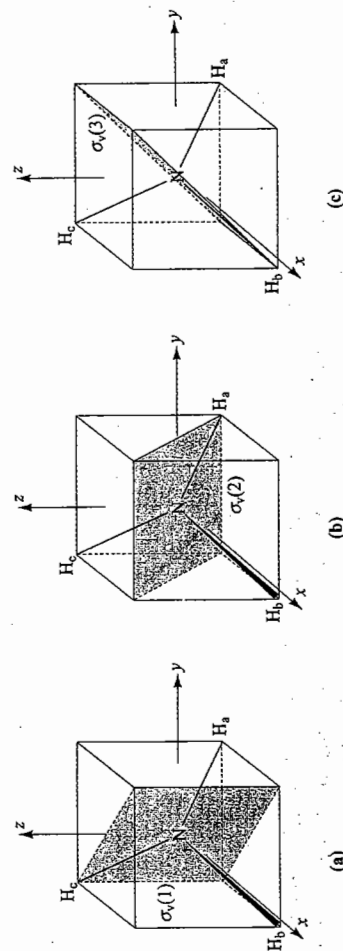


Fig. 5.5.4 Reflections in (a)  $\sigma_v(1)$  plane, (b)  $\sigma_v(2)$  plane, and (c)  $\sigma_v(3)$  plane

### Group Multiplication Table of the Point Group $C_{3v}$

The group multiplication table for the point group  $C_{3v}$  is shown in Table 5.5.2. The combinations shown within the square can be written straight-way as (i) the multiplication of an operation with an identity operation leaves it unchanged, and (ii) the operations  $C_3, C_3^2 (= C_3^{-1}), C_3^2 C_3 (= C_3^3) = E, \sigma_v(1)\sigma_v(1) [= \sigma_v(1)^2], \sigma_v(2)\sigma_v(2) [= \sigma_v(2)^2]$  and  $\sigma_v(3)\sigma_v(3) [= \sigma_v(3)^2]$  are equivalent to the identity operation. The remaining 18 combinations can be worked out either by carrying out the operations in the order shown (starting from the operation written at the extreme right and proceeding one by one to the left) or by multiplication of the corresponding matrices.

Table 5.5.2 Group Multiplication Table for the Point Group  $C_{3v}$

$C_{3v}$	$E$	$C_3$	$C_3^2$	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_v(3)$
$E$	$E$	$C_3$	$C_3^2$	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_v(3)$
$C_3$	$C_3$	$E$	$C_3^2$	$\sigma_v(2)$	$\sigma_v(3)$	$\sigma_v(1)$
$C_3^2$	$C_3^2$	$C_3$	$E$	$\sigma_v(3)$	$\sigma_v(1)$	$\sigma_v(2)$
$\sigma_v(1)$	$\sigma_v(1)$	$\sigma_v(3)$	$\sigma_v(2)$	$E$	$C_3^2$	$C_3$
$\sigma_v(2)$	$\sigma_v(2)$	$\sigma_v(1)$	$\sigma_v(3)$	$C_3$	$E$	$C_3^2$
$\sigma_v(3)$	$\sigma_v(3)$	$\sigma_v(2)$	$\sigma_v(1)$	$C_3^2$	$C_3$	$E$

We now work out the combinations not shown within squares in Table 5.5.2. We include only  $H_a, H_b$  and  $H_c$  as their positions are changed in the operations. The position of N does not change in any operation.

- $\sigma_v(1) C_3 [H_a; H_b; H_c] \rightarrow \sigma_v(1) [H_c; H_a; H_b] \rightarrow [H_a; H_c; H_b] \equiv \sigma_v(2) [H_a; H_b; H_c]$

$$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \equiv \sigma_v(2)$$

In the matrix notation, we have

$$\sigma_v(1) C_3 = \sigma_v(2)$$

Hereafter, we describe the results of geometric operation only. The results may be verified by the multiplication of the corresponding matrices.

- $\sigma_v(2) C_3 [H_a; H_b; H_c] \rightarrow \sigma_v(2) [H_c; H_a; H_b] \rightarrow [H_c; H_b; H_a] \equiv \sigma_v(3) [H_a; H_b; H_c]$
- $\sigma_v(3) C_3 [H_a; H_b; H_c] \rightarrow \sigma_v(3) [H_c; H_a; H_b] \rightarrow [H_b; H_a; H_c] \equiv \sigma_v(1) [H_a; H_b; H_c]$
- $\sigma_v(1) C_3^2 [H_a; H_b; H_c] \rightarrow \sigma_v(1) [H_b; H_c; H_a] \rightarrow [H_c; H_b; H_a] \equiv \sigma_v(3) [H_a; H_b; H_c]$
- $\sigma_v(2) C_3^2 [H_a; H_b; H_c] \rightarrow \sigma_v(2) [H_b; H_c; H_a] \rightarrow [H_b; H_a; H_c] \equiv \sigma_v(1) [H_a; H_b; H_c]$
- $\sigma_v(3) C_3^2 [H_a; H_b; H_c] \rightarrow \sigma_v(3) [H_b; H_c; H_a] \rightarrow [H_a; H_c; H_b] \equiv \sigma_v(2) [H_a; H_b; H_c]$
- $C_3 \sigma_v(1) [H_a; H_b; H_c] \rightarrow C_3 [H_b; H_c; H_a] \rightarrow [H_c; H_a; H_b] \equiv \sigma_v(2) [H_a; H_b; H_c]$

- $C_2^3 \sigma_1(1) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]} \rightarrow C_2^3 \text{ [H}_b\text{:H}_a\text{:H}_c\text{]} \rightarrow \text{[H}_a\text{:H}_c\text{:H}_b\text{]} \equiv \sigma_1(2) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]}$
- $\sigma_1(2) \sigma_1(1) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]} \rightarrow \sigma_1(2) \text{ [H}_b\text{:H}_a\text{:H}_c\text{]} \rightarrow \text{[H}_b\text{:H}_c\text{:H}_a\text{]} \equiv C_2^3 \text{ [H}_a\text{:H}_b\text{:H}_c\text{]}$
- $\sigma_1(3) \sigma_1(1) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]} \rightarrow \sigma_1(3) \text{ [H}_b\text{:H}_a\text{:H}_c\text{]} \rightarrow \text{[H}_c\text{:H}_a\text{:H}_b\text{]} \equiv C_3 \text{ [H}_a\text{:H}_b\text{:H}_c\text{]}$
- $C_3 \sigma_1(2) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]} \rightarrow C_3 \text{ [H}_a\text{:H}_c\text{:H}_b\text{]} \rightarrow \text{[H}_b\text{:H}_a\text{:H}_c\text{]} \equiv \sigma_1(1) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]}$
- $C_2^3 \sigma_1(2) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]} \rightarrow C_2^3 \text{ [H}_a\text{:H}_c\text{:H}_b\text{]} \rightarrow \text{[H}_c\text{:H}_b\text{:H}_a\text{]} \equiv \sigma_1(3) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]}$
- $\sigma_1(1) \sigma_1(2) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]} \rightarrow \sigma_1(1) \text{ [H}_a\text{:H}_c\text{:H}_b\text{]} \rightarrow \text{[H}_c\text{:H}_a\text{:H}_b\text{]} \equiv C_3 \text{ [H}_a\text{:H}_b\text{:H}_c\text{]}$
- $\sigma_1(3) \sigma_1(2) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]} \rightarrow \sigma_1(3) \text{ [H}_a\text{:H}_c\text{:H}_b\text{]} \rightarrow \text{[H}_b\text{:H}_c\text{:H}_a\text{]} \equiv C_2^3 \text{ [H}_a\text{:H}_b\text{:H}_c\text{]}$
- $C_3 \sigma_1(3) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]} \rightarrow C_3 \text{ [H}_c\text{:H}_b\text{:H}_a\text{]} \rightarrow \text{[H}_a\text{:H}_c\text{:H}_b\text{]} \equiv \sigma_1(2) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]}$
- $C_2^3 \sigma_1(3) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]} \rightarrow C_2^3 \text{ [H}_c\text{:H}_b\text{:H}_a\text{]} \rightarrow \text{[H}_b\text{:H}_a\text{:H}_c\text{]} \equiv \sigma_1(1) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]}$
- $\sigma_1(1) \sigma_1(3) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]} \rightarrow \sigma_1(1) \text{ [H}_c\text{:H}_b\text{:H}_a\text{]} \rightarrow \text{[H}_b\text{:H}_c\text{:H}_a\text{]} \equiv C_2^3 \text{ [H}_a\text{:H}_b\text{:H}_c\text{]}$
- $\sigma_1(2) \sigma_1(3) \text{ [H}_a\text{:H}_b\text{:H}_c\text{]} \rightarrow \sigma_1(2) \text{ [H}_c\text{:H}_b\text{:H}_a\text{]} \rightarrow \text{[H}_c\text{:H}_a\text{:H}_b\text{]} \equiv C_3 \text{ [H}_a\text{:H}_b\text{:H}_c\text{]}$

**Characteristics of a Point Group** The entries in a group multiplication table are in agreement with the four characteristics of a group. These are highlighted in the following.

- Any combination of two or more elements of the collection must be equivalent to one element which is also a member of the collection.
- This property is satisfied. This may be verified from the group multiplication tables of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  described in Table 5.5.1 and 5.5.2, respectively.
- One element in the group must commute with all other members and leave them unchanged.

This property is also satisfied by the identity operation of a group

- Every member of a group has a reciprocal, which is also an element of the group. For example,  $C_2$  is a reciprocal operation of  $C_3$  in a point group  $C_{3v}$ . The planes of reflection is a reciprocal of itself.

- The associative law of multiplication holds good

This may be exemplified by the combination  $C_3\sigma_v(1)\sigma_v(3)$  of the point group  $C_{3v}$ .

(i)  $C_3\{\sigma_v(1)\sigma_v(3)\}$

$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$(ii) \{C_3\sigma_v(1)\}\sigma_v(3)$$

$$E \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Hence,  $C_3\{\sigma_v(1)\sigma_v(3)\} = \{C_3\sigma_v(1)\}\sigma_v(3) = E$ .

This may be extended to any number of combinations of members of a group

## 5.6 CLASSES OF SYMMETRY OPERATIONS

The elements of a group can be separated into smaller sets, known as classes. This is based on the similarity transformation defined as

$$B = X^{-1}AX$$

where  $A$ ,  $B$  and  $X$  are the elements of the group. This expression is stated as: ' $B$  is the similarity transform of  $A$  by  $X$ '. The elements  $A$  and  $B$  are said to be conjugate to each other.

If each element of a group is subjected to similarity transformation by each element of the group, then the elements are divided into several classes, such that no element belongs to more than one class. Thus, a complete set of elements which are conjugate to one another is called a class of the group. Also, if  $n$  and  $m$  are the elements of a group and one of its classes, respectively, then  $n/m$  is always an integer. For example, if a group contains 10 elements, then the classes can have 1, 2 and 5 elements.

We work out the classes in the point group  $C_{3v}$ . Its members are  $E$ ,  $C_3$ ,  $C_3^2$ ,  $\sigma_v(1)$ ,  $\sigma_v(2)$  and  $\sigma_v(3)$ . Based on the fact that  $E^{-1} = E$ ,  $C_3^{-1} = C_3^2$ ,  $C_3^2 = C_3$ ,  $\sigma_v(1)^{-1} = \sigma_v(1)$ ,  $\sigma_v(2)^{-1} = \sigma_v(2)$  and  $\sigma_v(3)^{-1} = \sigma_v(3)$  and using the group multiplication table, we carry out the similarity transformation on each element by each of the elements listed above.

*Similarity Transformation of E* We have

$$E^{-1}EE^{-1} = E^{-1}E = E$$

$$C_3^{-1} E C_3 = C_3^{-1} C_3 = E$$

$$G_3^{-1} E G_3^2 = G_3^{-1} G_3^2 = E$$

Since  $E$  is similarity transform to  $E$  itself, the element  $E$  belongs to a class of the group.

Similarly Transformation of  $C_3^1$  we have

$$E^{-1}C_3^1E = E^{-1}C_3^1 = C_3^1$$

$$\Gamma_3^{-1}\Gamma_3\Gamma_3^{-1}=\Gamma_3^{-1}\Gamma_3^2=\Gamma_3$$

$$G_3^{-2} G_3^1 G_3^2 = G_3^{-2} E = G_3^1 E = G_3^3$$

The similarity transformation of  $C_3^1$  always give  $C_3^1$  or  $C_3^2$ . Thus, the operations  $C_3^1$  and  $C_3^2$  belong to one class of the group  $C_{3v}$ .

*Similarity Transformation of  $C_3^2$*  We have

$$E^{-1}C_3^2E = EC_3^2 = C_3^2$$

$$C_3^{-1}C_3^2C_3^1 = C_3^2E = C_3^2$$

$$G_3^{-1} G_3^2 G_3^2 = G_3^{-1} G_3^1 = G_3^2$$

The similarity transformation of  $C_3^2$  always give  $C_3^1$  or  $C_3^2$ .

**Similarity Transformation of  $\sigma_v(1)$**  We have

$$E^{-1} \sigma_v(1) E = E \sigma_v(1) = \sigma_v(1) \quad \sigma_v(1) \sigma_v(1) \sigma_v(1) = \sigma_v(1) \quad E = \sigma_v(1)$$

$$C_3^{-1} \sigma_v(1) C_3 = C_3^2 \sigma_v(2) = \sigma_v(3) \quad \sigma_v(2) \sigma_v(1) \sigma_v(2) = \sigma_v(2) \quad C_3 = \sigma_v(3)$$

$$C_3^{-2} \sigma_v(1) C_3^2 = C_3 \sigma_v(3) = \sigma_v(2) \quad \sigma_v(3) \sigma_v(1) \sigma_v(3) = \sigma_v(3) \quad C_3^2 = \sigma_v(2)$$

The similarity transformation of  $\sigma_v(1)$  always gives  $\sigma_v(1)$  or  $\sigma_v(2)$  or  $\sigma_v(3)$ . Thus, the operations  $\sigma_v(1)$ ,  $\sigma_v(2)$  and  $\sigma_v(3)$  belong to one class of the group  $C_{3v}$ .

Similarly, it can be worked out that the similarity transformation of  $\sigma_v(2)$  or  $\sigma_v(3)$  results into either  $\sigma_v(1)$  or  $\sigma_v(2)$  or  $\sigma_v(3)$ .

The determination of classes in a group may be time consuming especially when the group contains larger number of elements. The following simple rules help deciding the classes in a group.

- The symmetry operations  $E$ ,  $i$  and  $\sigma_h$  are each in a class by themselves.
- The rotation operations  $C_n^k$  and  $C_n^{n-k}$  ( $= C_n^{-k}$ ) belong to the same class (a different class for each value of  $k$ ) provided there exists either a plane of symmetry containing the  $C_n$  axis or a  $C_2$  axis perpendicular to the  $C_n$  axis. If not, they belong to different classes.
- Two reflection operations  $\sigma$  and  $\sigma'$  belong to the same class provided a symmetry operation in the group throws all points on the  $\sigma'$  plane into corresponding points in the  $\sigma$  plane.

A similar rule holds good for two rotational operations  $C_n^k$  and  $C_n^{k'}$  (or  $S_n^k$  and  $S_n^{k'}$ ) about different rotational axes.

A few characteristics shown by classes may be highlighted here.

- Every element is conjugate with itself, i.e.  $A = X^{-1}AX$ . The element  $X$  may always be  $E$  or any other element which commutes with  $A$ . This follows from the expression

$$E = A^{-1}A = A^{-1}(X^{-1}AX) = (A^{-1}X^{-1})(AX) = (XA)^{-1}(AX)$$

- If  $A$  is conjugate with  $B$ , then,  $B$  is conjugate with  $A$ . This follows from the fact Let  $A = X^{-1}BX$ . Hence

$$Y^{-1}AY = Y^{-1}(X^{-1}BX)Y = Y^{-1}X^{-1}BXY = B \text{ if } Y^{-1}X = X \text{ and } Y = X^{-1}$$

- If  $A$  is conjugate with  $B$  and  $C$ , then  $B$  and  $C$  are conjugate with each other.
- The order (i.e. number of elements) of all classes must be integral factors of the order of the group.

## 5.7 A FEW REPRESENTATIONS OF SYMMETRY OPERATIONS OF A POINT GROUP

In Section 5.3, it was shown that the symmetry operations of a molecule can be expressed mathematically in the matrix notations. In this section, a few representations of symmetry operations in a point group are described.

### TRANSLATIONAL VECTORS AS A BASIS OF REPRESENTATION

The translational vectors attached to one or more atoms of a molecule may be taken as a basis for representation of symmetry operations in a point group. This is being illustrated by taking the examples of water and ammonia molecules.

### Example of H<sub>2</sub>O Molecule

Let a translational vector in  $y$ -direction be attached to each atom of a water molecule as shown in Fig. 5.7.1. This set of vectors is represented as  $T_y$ . The behaviour of this set of vectors on applying the symmetry operations of the point group  $C_{2v}$  is studied (Fig. 5.7.1).

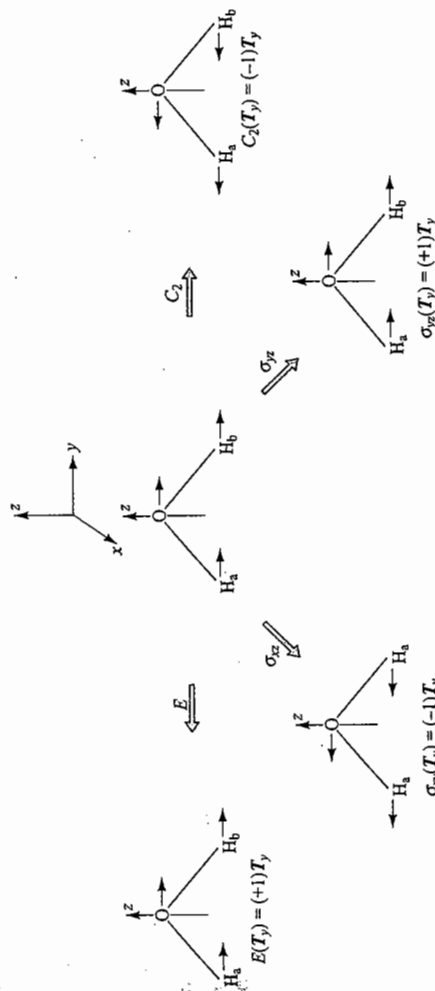


Fig. 5.7.1 Translational vectors  $T_y$  in  $H_2O$  molecule which lie in the  $yz$ -plane

It is found that the directions of the vectors either remain unchanged or show reversal of directions. This fact is expressed as follows.

$$E(T_y) = (+1)(T_y)$$

$$C_2(T_y) = (-1)(T_y)$$

$$\sigma_{xz}(T_y) = (-1)(T_y)$$

$$\sigma_{yz}(T_y) = (+1)(T_y)$$

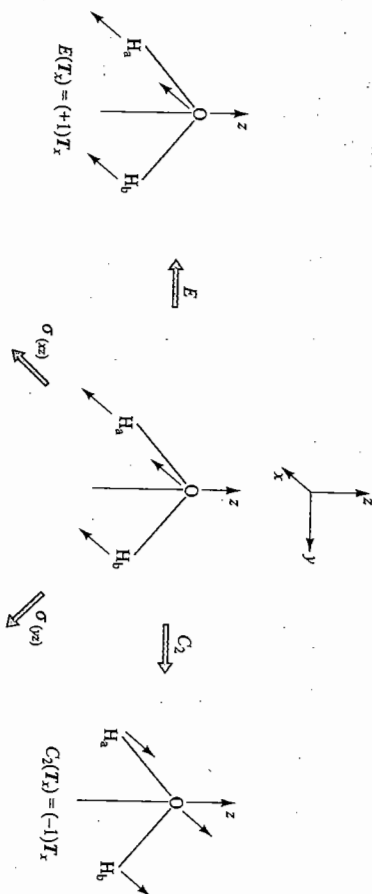
where +1 and -1 represent 'direction unchanged' and 'direction reversed', respectively. The above facts are shown in the following.

$C_{2v}$	$E$	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$	$T_y$
	+1	-1	-1	+1	

The above facts display one-dimensional representation of the point group  $C_{2v}$  for which translational vectors  $T_y$  form the basis. Similarly, one can obtain one-dimensional representations based on translational vectors  $T_x$  (see Fig. 5.7.2) and  $T_z$ . These along with  $T_y$  are shown in Table 5.7.1. The representations shown in Table 5.7.1 follow the group multiplication table given in Table 5.5.1 for the water molecule.

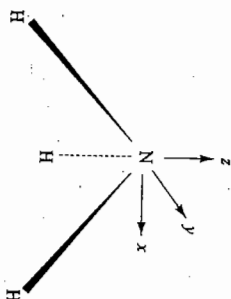
Table 5.7.1 One-dimensional Representations based on  $T_x$ ,  $T_y$  and  $T_z$

$C_{2v}$	$E$	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$	$T_x$	$T_y$	$T_z$
	+1	-1	+1	-1	-1	-1	-1
	+1	-1	-1	+1	-1	+1	+1
	+1	+1	+1	+1	+1	+1	+1

Fig. 5.7.2 Translational vectors  $T_x$  in water molecule

### Example of Ammonia Molecule

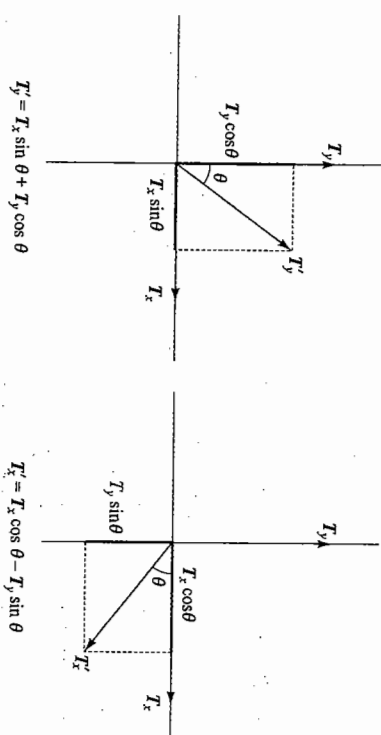
Ammonia molecule belongs to the point group  $C_{3v}$ . A set of Cartesian axes is located on nitrogen atom with the rotational axis  $C_3$  coinciding with the  $z$ -axis (Fig. 5.7.3).

Fig. 5.7.3 Cartesian axes on N atom in  $NH_3$ 

Let the translational vectors  $T_x$ ,  $T_y$  and  $T_z$  be placed on the nitrogen atom along the  $x$ -,  $y$ - and  $z$ -axes, respectively. The behaviour of these vectors is studied when the molecule is subjected to the symmetry operations of the point group  $C_{3v}$ .

Let the molecule be rotated clockwise about the  $z$ -axis. Viewing the molecule down the main symmetry axis (i.e.  $z$ -axis), the new positions of translational vectors  $T'_x$  and  $T'_y$  are shown in Fig. 5.7.4. These vectors can be expressed in terms of original translational vectors  $T_x$  and  $T_y$  as described in the following.

Fig. 5.7.4 Effect of rotation on translational vectors



$$T'_y = T_x \sin \theta + T_y \cos \theta$$

$$T'_x = T_x \cos \theta - T_y \sin \theta$$

The vector  $T'_x$  is obtained by the vector subtraction of  $T_y \sin \theta$  from  $T_x \cos \theta$ , i.e.

$$T'_x = T_x \cos \theta - T_y \sin \theta \quad (5.7.1)$$

The vector  $T'_y$  is obtained by the vector addition of  $T_x \sin \theta$  and  $T_y \cos \theta$ , i.e.

$$T'_y = T_x \sin \theta + T_y \cos \theta \quad (5.7.2)$$

In the matrix notations, Eqs (5.7.1) and (5.7.2) are expressed as

$$\begin{pmatrix} T'_x \\ T'_y \end{pmatrix} = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} T_x \\ T_y \end{pmatrix} \quad (5.7.3)$$

that is, the effect of rotation on  $NH_3$  molecule is represented by a  $2 \times 2$  transformation matrix<sup>†</sup> as described in Eq. (5.7.3).

Now, we describe the transformation matrices for the symmetry operations of the point group  $C_{3v}$ .

Since the vectors  $T_x$  and  $T_y$  remain unshifted, the transformation matrix of this operation is  $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ .

The angle  $\theta$  in this rotation is  $120^\circ$ . Hence, the transformation matrix is

$$\begin{pmatrix} \cos 120^\circ & -\sin 120^\circ \\ \sin 120^\circ & \cos 120^\circ \end{pmatrix} \quad \text{i.e.} \quad \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$$

<sup>†</sup>During the rotation of  $NH_3$  molecule about  $z$ -axis, the translation vector  $T_z$  remains unshifted. We may include this effect by writing  $3 \times 3$  transformation matrix as

$$\begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{This matrix may be factored as} \quad \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \quad \text{and} \quad (1)$$

Since the translational vector  $T_z$  is not mixed up with  $T_x$  and  $T_y$  under any symmetry operation and the fact that  $T_x$  and  $T_y$  mix each other, we describe only  $2 \times 2$  transformation matrices for the various symmetry operations of the point group  $C_{3v}$ .

**$C_3^2$  Operation**

The angle  $\theta$  in this operation is  $240^\circ$ . Hence, the transformation matrix is

$$\begin{pmatrix} \cos 240^\circ & -\sin 240^\circ \\ \sin 240^\circ & \cos 240^\circ \end{pmatrix} \text{ i.e. } \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$$

The reflection plane  $\sigma_v(1)$  of  $\text{NH}_3$  molecule, when viewed down the z-axis, is shown in Fig. 5.7.5.

 **$\sigma_v(1)$  Operation**

During reflection, the vector  $T_x$  remains unaffected while the vector  $T_y$  shows reversal of direction. Hence, the transformation matrix† is

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

 **$\sigma_v(2)$  Operation**

The reflection plane  $\sigma_v(2)$  of  $\text{NH}_3$  molecule, when viewed down the z-axis, is shown in Fig. 5.7.6.

The reflection of the vector  $T_x$  is equivalent to rotating it by an angle  $120^\circ$  clockwise and that of  $T_y$  is equivalent to rotating it by an angle  $60^\circ$  (anticlockwise) or  $300^\circ$  (clockwise). Hence, the transformation matrix is

$$\begin{pmatrix} \cos 120^\circ & -\sin 120^\circ \\ \sin 300^\circ & \cos 300^\circ \end{pmatrix} \text{ i.e. } \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix}$$

 **$\sigma_v(3)$  Operation**

The reflection plane  $\sigma_v(3)$  of  $\text{NH}_3$  molecule, when viewed down the z-axis, is shown in Fig. 5.7.7.

The reflection of the vector  $T_x$  is equivalent to rotating it by an angle  $120^\circ$  (anticlockwise) or  $240^\circ$  (clockwise) and that of  $T_y$  is equivalent to rotating it by an angle  $60^\circ$  (clockwise). Hence, the transformation matrix is

$$\begin{pmatrix} \cos 240^\circ & -\sin 240^\circ \\ \sin 60^\circ & \cos 60^\circ \end{pmatrix} \text{ i.e. } \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}$$

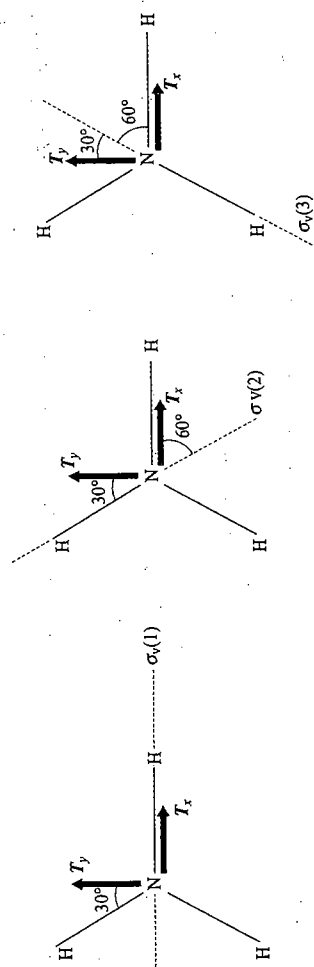


Fig. 5.7.5 Reflection plane  $\sigma_v(1)$  Fig. 5.7.6 Reflection plane  $\sigma_v(2)$  Fig. 5.7.7 Reflection plane  $\sigma_v(3)$

Note: The reflection  $\sigma_v(1)$  is equivalent to rotating (i) the vector  $T_x$  by  $0^\circ$ , and (ii) the vector  $T_y$  by  $180^\circ$ . Hence, the transformation matrix is

$$\begin{pmatrix} \cos 0^\circ & -\sin 0^\circ \\ \sin 180^\circ & \cos 180^\circ \end{pmatrix} \text{ i.e. } \begin{pmatrix} +1 & 0 \\ 0 & -1 \end{pmatrix}$$

Table 5.7.2 displays the representations of the point group  $C_{3v}$  based on the translational vectors located on the N atom.

Note: The representations shown in Table 5.7.2 follow the group multiplication table given in Table 5.5.2 for the  $\text{NH}_3$  molecule.

Table 5.7.2 Representation of the Point Group  $C_{3v}$  based on Translational Vectors

$C_{3v}$	$E$	$C_3$	$C_3^2$	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_v(3)$	$T_z$
1	1	1	1	1	1	1	$(T_x, T_y)$
	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}$	

**ROTATIONAL VECTORS AS A BASIS OF REPRESENTATION**

**Example of  $\text{H}_2\text{O}$  Molecule** Let the water molecule shown in Fig. 5.7.8 be rotated about the z-axis. The rotational vectors associated with atoms  $\text{H}_a$  and  $\text{H}_b$  lie in xy plane. Their behaviour under symmetry operations of the point group  $C_{2v}$  is also displayed in Fig. 5.7.8.

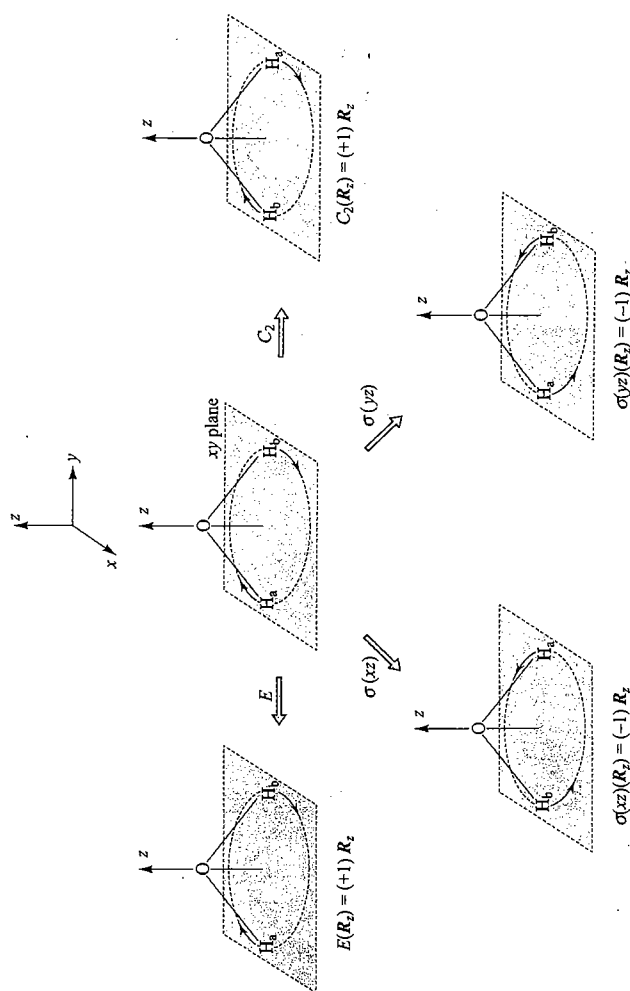


Fig. 5.7.8 Rotational vectors  $R_z$  in  $\text{H}_2\text{O}$  molecule

It is found that the rotational vectors either remain unchanged or show reversal of directions. These facts are expressed as

$$\begin{aligned} E(R_z) &= (+1)R_z \\ C_2(R_z) &= (+1)R_z \\ \sigma_v(xz)(R_z) &= (-1)R_z \\ \sigma_v(yz)(R_z) &= (-1)R_z \end{aligned}$$

where +1 and -1 represent 'direction unchanged' and 'direction reversed', respectively. The above facts are shown in the following.

$C_{2v}$	$E$	$C_2$	$\sigma_x$	$\sigma_y$	$R_z$
	1	1	-1	-1	

The above facts display one-dimensional representation of the point group  $C_{2v}$ . This is based on the rotational vectors  $R_z$ . Similarly, one can work out one-dimensional representations based on  $R_x$  (see, Fig. 5.7.9) and  $R_y$  (see, Fig. 5.7.10).

The rotational vectors  $R_x$  lie in the  $yz$  plane and both the vectors (attached to  $H_a$  and  $H_b$ ) have identical orientations and originate tangentially from their respective  $-y$  direction. Consequently, the rotational vectors  $R_x$  and the translational vectors  $T_y$  behave in identical manner under the symmetry operations and thus produce exactly identical one-dimensional representations.

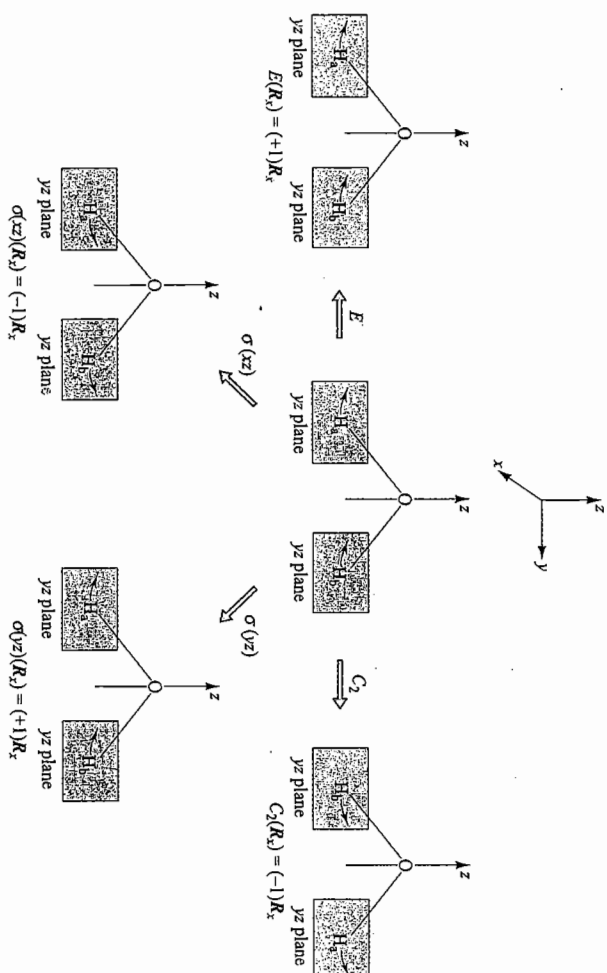
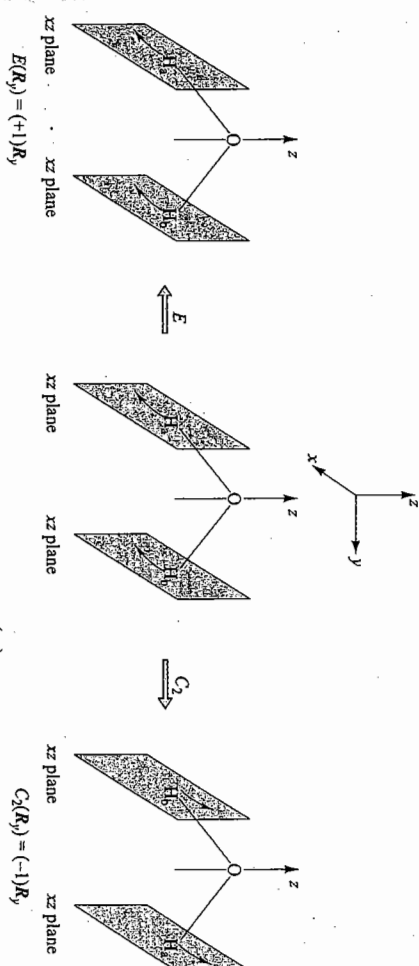


Fig. 5.7.9 Behaviour of  $R_x$  under symmetry operations



5.7.10 Behaviour of  $R_y$  under symmetry operations

The rotational vectors  $R_y$  lie in the  $xz$  plane and both the vectors (attached to  $H_a$  and  $H_b$ ) have identical orientations and originate tangentially from their respective  $+x$  direction. Consequently, the rotational vectors  $R_y$  and the translational vectors  $T_x$  behave in identical manner under the symmetry operation and thus produce exactly identical one-dimensional representations.

Table 5.7.3 displays one-dimensional representations of the point group  $C_{2v}$  based on the  $R_x$  and  $R_y$  vectors along with that of the  $R_z$  vectors.

Table 5.7.3 One-dimensional Representations based on the Rotational Vectors

$C_{2v}$	$E$	$C_2$	$\sigma_x$	$\sigma_y$	$R_z$ (behaves like $T_z$ )	$R_x$ (behaves like $T_y$ )	$R_y$ (behaves like $T_x$ )
	1	-1	-1	1	1	1	1
	1	-1	1	-1	1	-1	-1
	1	1	-1	-1	1	1	-1

### Example of NH<sub>3</sub> Molecule

The top view of ammonia molecule when look down the +z axis is shown in Fig. 5.7.11. The rotational vectors  $R_z$  attached to the three hydrogen atoms, when the molecule is rotated about the z-axis, are also shown in Fig. 5.7.11. Their behaviour under symmetry operations of the point group  $C_{3v}$  is shown in the following.

$C_{3v}$	$E$	$C_3$	$C_3^2$	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_v(3)$	$R_z$
	1	1	1	-1	-1	-1	

When the molecule is rotated about the x-axis, the three hydrogen atoms rotate in their respective yz plane and the rotation vectors originate tangentially from their respective y-direction. Consequently, the rotational vectors  $R_x$  and the translational vectors  $T_y$  behave in identical manner under the symmetry operations and produce exactly identical two-dimensional representations.

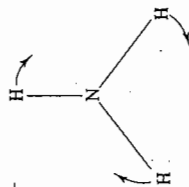


Fig. 5.7.11 Top view of ammonia

When the ammonia molecule is rotated about the y-axis, the rotational vectors  $R_y$  attached to each of the three hydrogen atoms lie in their respective xz planes and originate tangentially from the respective x-direction, respectively. Consequently, the rotational vectors  $R_y$  and the translational vectors  $T_x$  behave in identical manner under the symmetry operations and produce exactly identical two-dimensional representations.

Table 5.7.4 displays the representations of the point group  $C_{3v}$  based on the  $R_x$  and  $R_y$  vectors along with that of the  $R_z$  vectors.

Table 5.7.4 Representations of the Point Group  $C_{3v}$  based on Rotational Vectors

$C_{3v}$	$E$	$C_3$	$C_3^2$	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_v(3)$	$R_z$
	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$	$(R_x, R_y)$

### BOND VECTORS AS A BASIS OF REPRESENTATIONS

The set of bond vectors may be taken as the basis of representations of symmetry operations of a point group. This is being illustrated by taking the examples of water and ammonia molecules.

Example of Water Molecule

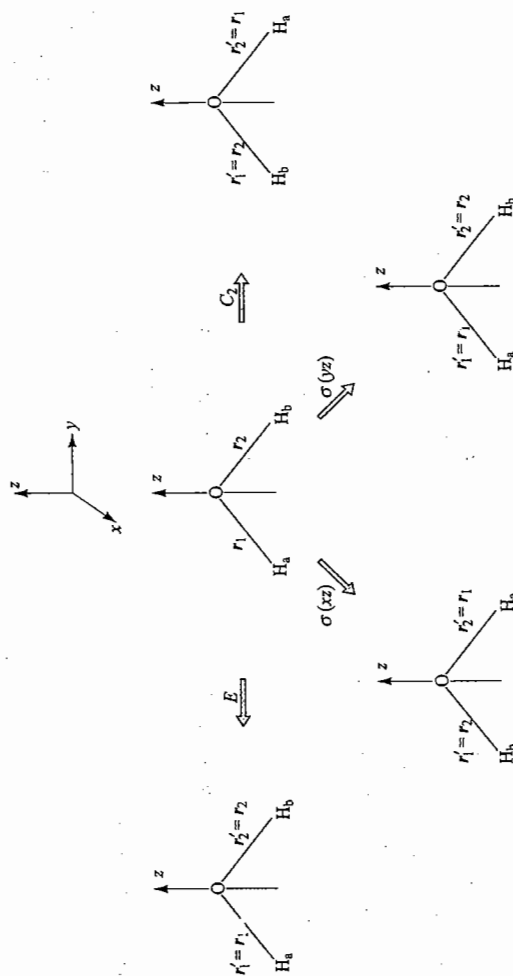


Fig. 5.7.12 Behaviour of bond vectors under symmetry operations applied to H<sub>2</sub>O

If we carry out the symmetry operations of  $C_{2v}$  on these two vectors, we obtain the following facts.

**Identity operation** we have  $\sigma(xz)$  operation we have

$$\begin{pmatrix} r'_1 \\ r'_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix} \quad \begin{pmatrix} r'_1 \\ r'_2 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}$$

**C<sub>2</sub> operation** we have

$$\begin{pmatrix} r'_1 \\ r'_2 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix} \quad \sigma'_{yz} \text{ operation we have}$$

$$\begin{pmatrix} r'_1 \\ r'_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \end{pmatrix}$$

Hence, the transformation matrices of the point group  $C_{2v}$  are as follows.

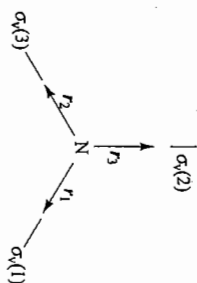
**Transformation Matrices**

$C_{2v}$	$E$	$C_2$	$\sigma(xz)$	$\sigma(yz)$
	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

**Example of Ammonia Molecule**

Figure 5.7.13 displays the bond vectors in  $\text{NH}_3$  molecule as viewed from the top of the molecule.

Fig. 5.7.13 Bond vectors in  $\text{NH}_3$  (viewed from top,  $C_3$  axis lies perpendicular to plane of paper passing through N atom)



If we carry out the symmetry operations of  $C_{3v}$  on these three vectors, we obtain the following facts.

**Identity operation** we have

$$\begin{pmatrix} r'_1 \\ r'_2 \\ r'_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$$

**$C_3^2$  operations** we have

$$\begin{pmatrix} r'_1 \\ r'_2 \\ r'_3 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$$

**$\sigma_v(2)$  operation** we have

$$\begin{pmatrix} r'_1 \\ r'_2 \\ r'_3 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$$

**$C_3^1$  operation** we have

$$\begin{pmatrix} r'_1 \\ r'_2 \\ r'_3 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$$

**$\sigma_v(1)$  operation** we have

$$\begin{pmatrix} r'_1 \\ r'_2 \\ r'_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$$

**$\sigma_v(3)$  operation** we have

$$\begin{pmatrix} r'_1 \\ r'_2 \\ r'_3 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$$

The transformation matrices of the point group  $C_{3v}$  are as follows.

$C_{3v}$	$E$	$C_3^1$	$C_3^2$	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_v(3)$
	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

**ATOMIC WAVE FUNCTIONS AS A BASIS OF REPRESENTATIONS**

Atomic wave functions (i.e. atomic orbitals) may be taken as the basis of representations of symmetry operations of a point group. One can write out the atomic functions explicitly (or the angular part only since the radial part is unaltered by all symmetry operations) and determine the effect of performing symmetry

operation on it. Alternatively, the effects may be visualized by carrying out the symmetry operation on the orbital diagrams. We illustrate these by taking the examples  $\text{H}_2\text{O}$  and  $\text{SO}_2$  for the point group  $C_{2v}$  and  $\text{NH}_3$  and  $\text{PCl}_3$  from the point group  $C_{3v}$ .

**POINT GROUP  $C_{2v}$** **EXAMPLE OF p ORBITALS (WATER MOLECULE)**

Considering the p orbitals of oxygen, we write their angular wave functions as

$$P_x = \sin \theta \cos \varphi, \quad P_y = \sin \theta \sin \varphi \quad \text{and} \quad P_z = \cos \theta$$

**Note:** The subscript to the orbital p corresponds to the respective angular dependence.

The various operations of the point group  $C_{2v}$  have the following effects on angle  $\theta$  and  $\varphi$  (see Fig. 5.7.14).

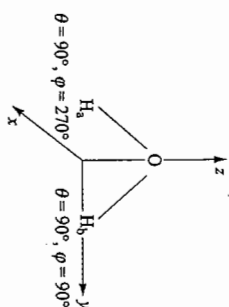


Fig. 5.7.14 Orientation of water molecule

**Effects on Angles  $\theta$  and  $\varphi$  by Symmetry Operations**

**Identity operation** No effect on  $\theta$  and  $\varphi$ .

**Rotation (clockwise) operation** If the rotation axis coincides with the z-axis (Fig. 5.7.14), then  $\theta$  remain unaltered and  $\varphi$  changes to  $\varphi - 360^\circ/n$ , where  $n$  is the order of rotational axis.

**Reflection operations**

$\sigma_x$  plane:  $\theta$  remains the same,  $\varphi$  changes to  $-\varphi$

$\sigma_{yz}$  plane:  $\theta$  remains the same,  $\varphi$  changes to  $180^\circ - \varphi$

$\sigma_{xz}$  plane:  $\theta$  changes to  $180^\circ - \theta$ ,  $\varphi$  remains the same

The effect on  $\cos \varphi$  and  $\sin \varphi$  are as follows.

**$C_2$  Operation**  $C_2 \cos \varphi = \cos(\varphi - 180^\circ) = -\cos \varphi$

$$C_2 \sin \varphi = \sin(\varphi - 180^\circ) = -\sin \varphi$$

**$\sigma_x$  Operation**

$$\sigma_x \cos \varphi = \cos(-\varphi) = \cos \varphi$$

$$\sigma_x \sin \varphi = \sin(-\varphi) = -\sin \varphi$$

**$\sigma_{yz}$  Operation**

$$\sigma_{yz} \cos \varphi = \cos(180^\circ - \varphi) = -\cos \varphi$$

$$\sigma_{yz} \sin \varphi = \sin(180^\circ - \varphi) = \sin \varphi$$



### Effect on $p_x$ Orbital

The effect on  $p_x$  orbitals are as follows.

$$\begin{aligned}
 E(p_x) &= (+1)p_x \\
 C_2(p_x) &= C_2(\sin \theta \cos \varphi) = -\sin \theta \cos \varphi = (-1)p_x \\
 \sigma_{xz}(p_x) &= \sigma_{xz}(\sin \theta \cos \varphi) = \sin \theta \cos \varphi = (+1)p_x \\
 \sigma_{yz}(p_x) &= \sigma_{yz}(\sin \theta \cos \varphi) = -\sin \theta \cos \varphi = (-1)p_x \\
 E(p_y) &= (+1)p_y \\
 C_2(p_y) &= C_2(\sin \theta \sin \varphi) = -\sin \theta \sin \varphi = (-1)p_y \\
 \sigma_{xz}(p_y) &= \sigma_{xz}(\sin \theta \sin \varphi) = -\sin \theta \sin \varphi = (-1)p_y \\
 \sigma_{yz}(p_y) &= \sigma_{yz}(\sin \theta \sin \varphi) = \sin \theta \sin \varphi = (+1)p_y
 \end{aligned}$$

Since  $p_z$  orbital does not include angle  $\varphi$ , we will have

$$\begin{aligned}
 E(p_z) &= (+1)p_z; \\
 \sigma_{xz}(p_z) &= (+1)p_z; \\
 \sigma_{yz}(p_z) &= (+1)p_z
 \end{aligned}$$

The above facts can also be visualized by carrying out the symmetry operations on the orbital diagrams of  $p_x$ ,  $p_y$  and  $p_z$  orbital. Figure 5.7.15 displays these effects for  $p_x$  and  $p_y$  orbitals.

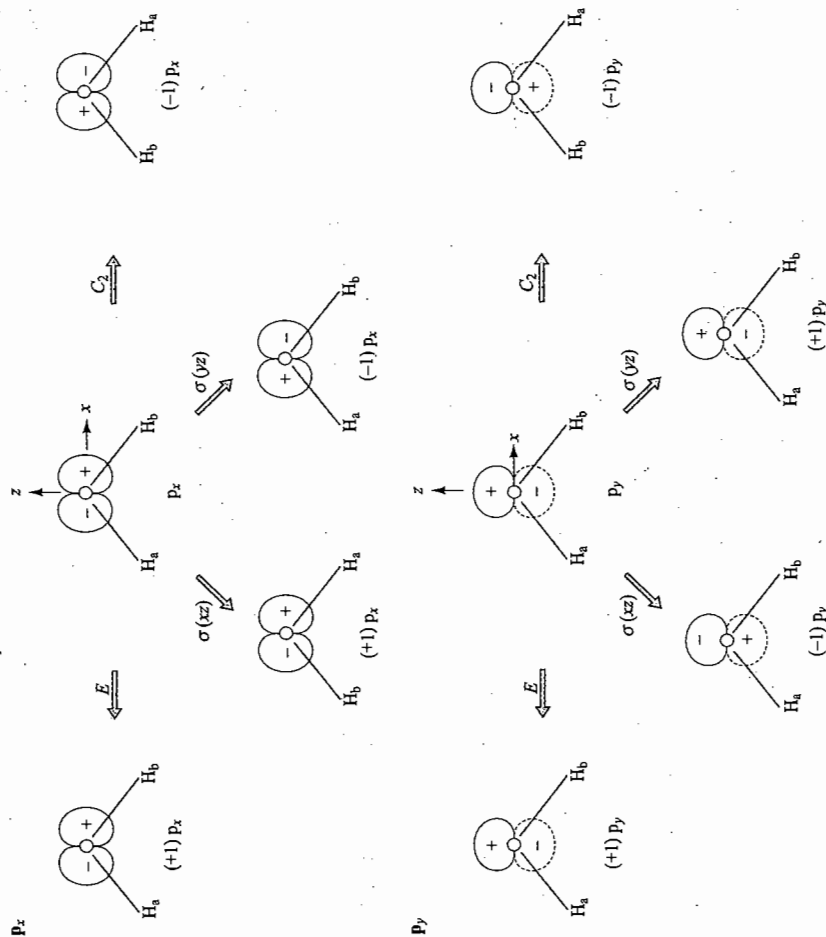


Fig. 5.7.15 Effect of symmetry operations on  $p_x$  and  $p_y$  orbitals of oxygen in water

### Transformation Matrices

The transformation matrices (which is  $1 \times 1$ ) of the point group  $C_{2v}$  based on  $p$  orbitals are as follows

$C_{2v}$	$E$	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$	
	+1	+1	+1	+1	$p_z$
	+1	-1	+1	-1	$p_x$
	+1	-1	-1	+1	$p_y$

### EXAMPLES OF d ORBITALS (SULPHUR DIOXIDE MOLECULE)

Considering the  $d$  orbitals of sulphur in  $SO_2$ , we write the angular portions of these orbitals.

$$\begin{aligned}
 d_{2z^2-x^2-y^2} &= d_{z^2} = 3 \cos^2 \theta - 1 & d_{xz} &= \sin \theta \cos \varphi \\
 d_{x^2-y^2} &= \sin^2 \theta \cos 2\varphi & d_{yz} &= \sin \theta \sin \varphi \\
 d_{xy} &= \sin^2 \theta \sin 2\varphi
 \end{aligned}$$

**Note:** The subscripts to the  $d$  orbitals correspond to the respective angular dependence. Exception is  $d_{z^2}$  which actually corresponds to  $d_{2z^2-x^2-y^2}$ .

The effects on  $\cos 2\varphi$  and  $\sin 2\varphi$  are as follows.

$$\begin{aligned}
 C_2 \text{ Operation } C_2(\cos 2\varphi) &= \cos 2(\varphi - 180^\circ) = \cos 2\varphi \\
 C_2(\sin 2\varphi) &= \sin 2(\varphi - 180^\circ) = \sin 2\varphi \\
 \sigma_{xz} \text{ Operation } \sigma_{xz}(\cos 2\varphi) &= \cos \{2(-\varphi)\} = \cos 2\varphi \\
 \sigma_{xz}(\sin 2\varphi) &= \sin \{2(-\varphi)\} = -\sin 2\varphi \\
 \sigma_{yz} \text{ Operation } \sigma_{yz}(\cos 2\varphi) &= \cos 2(180^\circ - \varphi) = \cos 2\varphi \\
 \sigma_{yz}(\sin 2\varphi) &= \sin 2(180^\circ - \varphi) = -\sin 2\varphi
 \end{aligned}$$

With these, the effect on  $d$  orbitals are as follows.

Since  $d_{z^2}$  orbital does not include  $\varphi$ -dependent term, we will have

$$\begin{aligned}
 E(d_{z^2}) &= (+1)d_{z^2} & C_2(d_{z^2}) &= (+1)d_{z^2} \\
 \sigma_{xz}(d_{z^2}) &= (+1)d_{z^2} & \sigma_{yz}(d_{z^2}) &= (+1)d_{z^2}
 \end{aligned}$$

$$\begin{aligned}
 E(d_{x^2-y^2}) &= E(\sin^2 \theta \cos 2\varphi) = \sin^2 \theta \cos 2\varphi = (+1)d_{x^2-y^2} \\
 C_2(d_{x^2-y^2}) &= C_2(\sin^2 \theta \cos 2\varphi) = \sin^2 \theta \cos 2\varphi = (+1)d_{x^2-y^2} \\
 \sigma_{xz}(d_{x^2-y^2}) &= \sigma_{xz}(\sin^2 \theta \cos 2\varphi) = \sin^2 \theta \cos 2\varphi = (+1)d_{x^2-y^2} \\
 \sigma_{yz}(d_{x^2-y^2}) &= \sigma_{yz}(\sin^2 \theta \cos 2\varphi) = \sin^2 \theta \cos 2\varphi = (+1)d_{x^2-y^2}
 \end{aligned}$$

$$\begin{aligned}
 E(d_{xy}) &= E(\sin^2 \theta \sin 2\varphi) = \sin^2 \theta \sin 2\varphi = (+1)d_{xy} \\
 C_2(d_{xy}) &= C_2(\sin^2 \theta \sin 2\varphi) = \sin^2 \theta \sin 2\varphi = (+1)d_{xy}
 \end{aligned}$$

$$\begin{aligned}
 \sigma_{xz}(d_{xy}) &= \sigma_{xz}(\sin^2 \theta \sin 2\varphi) = -\sin^2 \theta \sin 2\varphi = (-1)d_{xy} \\
 \sigma_{yz}(d_{xy}) &= \sigma_{yz}(\sin^2 \theta \sin 2\varphi) = -\sin^2 \theta \sin 2\varphi = (-1)d_{xy}
 \end{aligned}$$

$$\begin{aligned}
 E(d_{xz}) &= E(\sin \theta \cos \varphi) = \sin \theta \cos \varphi = (+1)d_{xz} \\
 C_2(d_{xz}) &= C_2(\sin \theta \cos \varphi) = -\sin \theta \cos \varphi = (-1)d_{xz}
 \end{aligned}$$

Effect on  $d_{yz}$  Orbital

$$\begin{aligned}\sigma_x(d_{yz}) &= \sigma_x(\sin \theta \cos \theta \cos \phi) = \sin \theta \cos \theta \cos \phi = (+1)d_{yz} \\ \sigma_y(d_{yz}) &= \sigma_y(\sin \theta \cos \theta \cos \phi) = -\sin \theta \cos \theta \cos \phi = (-1)d_{yz} \\ E(d_{yz}) &= E(\sin \theta \cos \theta \sin \phi) = \sin \theta \cos \theta \sin \phi = (+1)d_{yz} \\ C_2(d_{yz}) &= C_2(\sin \theta \cos \theta \sin \phi) = -\sin \theta \cos \theta \sin \phi = (-1)d_{yz} \\ \sigma_x(d_{yz}) &= \sigma_x(\sin \theta \cos \theta \sin \phi) = -\sin \theta \cos \theta \sin \phi = (-1)d_{yz} \\ \sigma_y(d_{yz}) &= \sigma_y(\sin \theta \cos \theta \sin \phi) = \sin \theta \cos \theta \sin \phi = (+1)d_{yz}\end{aligned}$$

The above facts can also be visualized by carrying out the symmetry operations on the d-orbital diagrams. Figure 5.7.16 displays these effects for  $d_{x^2-y^2}$ ,  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals.

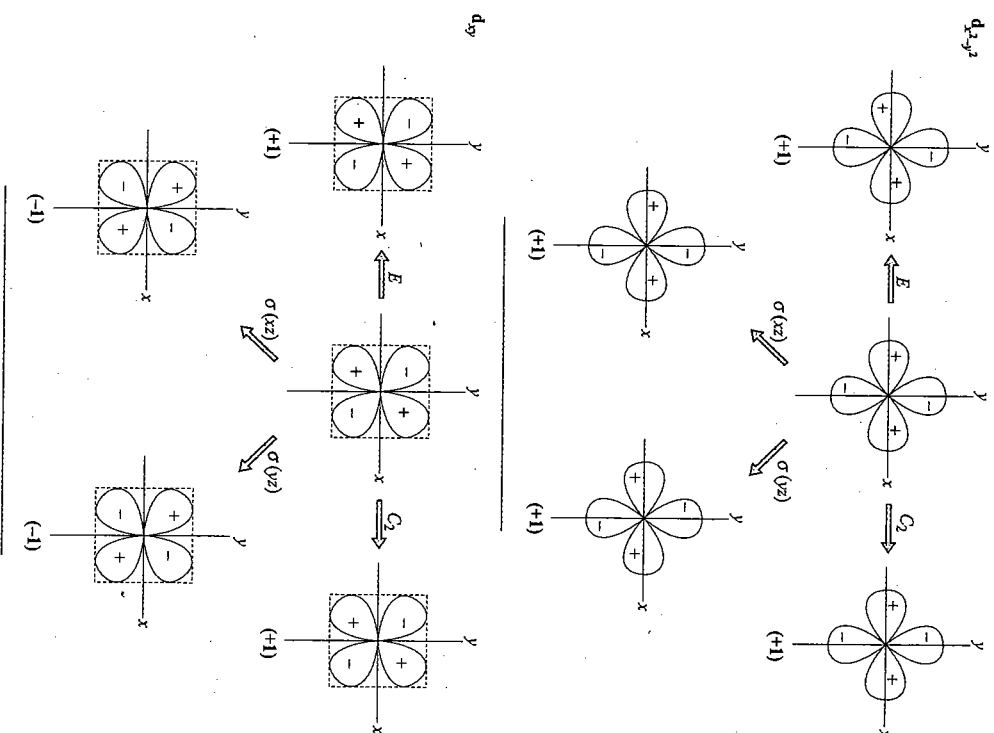
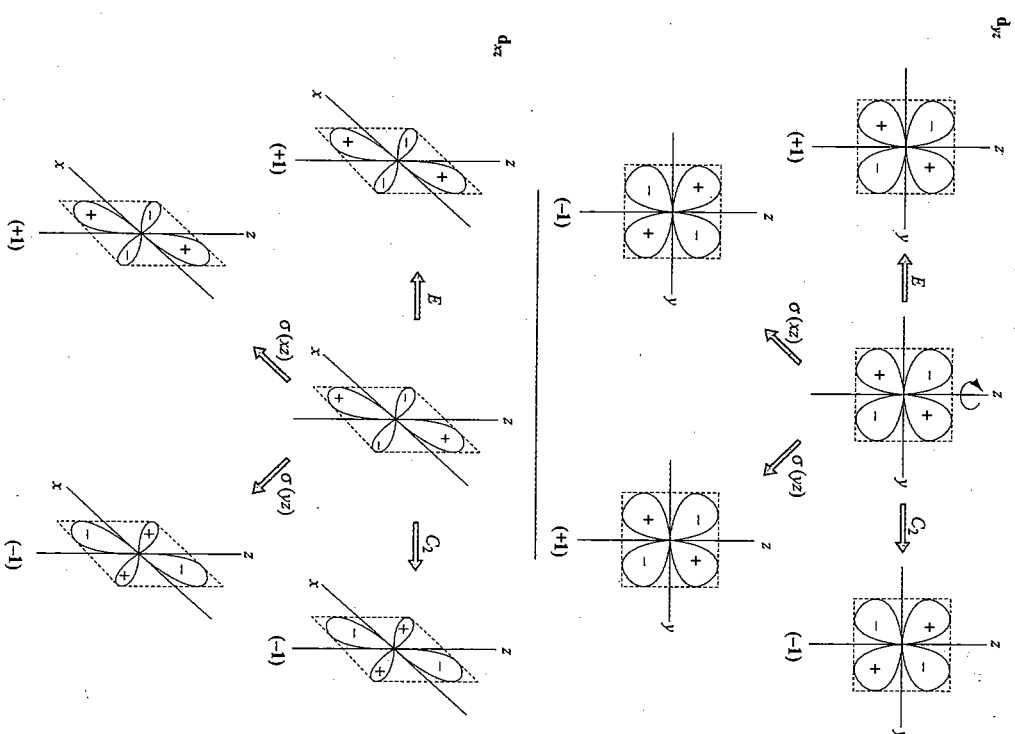


Fig. 5.7.16 (continued)

Fig. 5.7.16 Effect of symmetry operations on d orbital of sulphur in  $\text{SO}_2$ 

## Transformation Matrices

The transformation matrices (each one is  $1 \times 1$ ) of the point group  $C_{2v}$  based on d orbitals are as follows.

$C_{2v}$	$E$	$C_{2v}$	$\sigma_{xz}$	$\sigma_{yz}$	
	+1	+1	+1	+1	$d_{z^2}, d_{x^2-y^2}$
	+1	+1	-1	-1	$d_{xy}$
	+1	-1	+1	-1	$d_{xz}$
	+1	-1	-1	+1	$d_{yz}$

POINT GROUP  $C_{3v}$ 

## EXAMPLE OF p ORBITALS (AMMONIA MOLECULE)

Considering the p orbitals of nitrogen, we have

$$-p_x = \sin \theta \cos \varphi; \quad p_y = \sin \theta \sin \varphi; \quad p_z = \cos \theta$$

**Effect on  $\theta$  and  $\varphi$**  For the various operations of the point group  $C_{3v}$ , we have the following effects on angle  $\theta$  and  $\varphi$ .

**Identity operation** No effect on  $\theta$  and  $\varphi$ .

**Rotation operation** If the rotation axis coincides with the z-axis, (see, Fig. 5.7.17), then

$\theta$  remains constant

$\varphi$  changes to  $\varphi - m \times 360^\circ/n$ , where  $n$  is the order of rotation axis,  $m$  is the number of times the rotation applies

Thus, For  $C_3$ ,  $\varphi$  changes to  $\varphi - 120^\circ$  and for  $C_3^2$ ,  $\varphi$  changes to  $\varphi - 240^\circ$ .

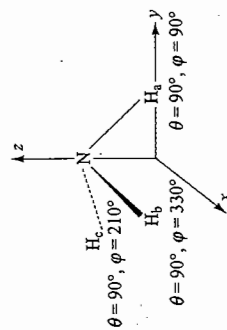


Fig. 5.7.17  
Orientation of  $\text{NH}_3$   
molecule

**Reflection operations** Let the bond  $\text{N}-\text{H}_a$  lies in the  $yz$ -plane (Fig. 5.7.17). During reflection, angle  $\theta$  remains the same while the angle  $\varphi$  undergoes the following changes.

$$\begin{aligned} \sigma_{yz} &= \sigma_{\text{NH}_a} & \varphi \text{ changes to } 180^\circ - \varphi \\ \sigma_{\text{NH}_b} & & \varphi \text{ changes to } 60^\circ - \varphi, \text{ i.e. } 300^\circ - \varphi \\ \sigma_{\text{NH}_c} & & \varphi \text{ changes to } 420^\circ - \varphi, \text{ i.e. } 60^\circ - \varphi \end{aligned}$$

The effect on  $\cos \varphi$  and  $\sin \varphi$  are as follows.

$$C_3 \text{ Operation} \quad \cos(\varphi - 120^\circ) = -\sin(30^\circ - \varphi) = -\frac{1}{2} \cos \varphi + \frac{\sqrt{3}}{2} \sin \varphi$$

$$\sin(\varphi - 120^\circ) = -\sin(60^\circ + \varphi) = -\frac{\sqrt{3}}{2} \cos \varphi - \frac{1}{2} \sin \varphi$$

$C_3^2$  Operation

$$\cos(\varphi - 240^\circ) = -\cos(60^\circ - \varphi) = -\frac{1}{2} \cos \varphi - \frac{\sqrt{3}}{2} \sin \varphi$$

$$\sin(\varphi - 240^\circ) = \sin(60^\circ - \varphi) = \frac{\sqrt{3}}{2} \cos \varphi - \frac{1}{2} \sin \varphi$$

$\sigma_{\text{NH}_a}$  Operation

$$\cos(180^\circ - \varphi) = -\cos \varphi$$

$$\sin(180^\circ - \varphi) = \sin \varphi$$

**Effect on  $\cos \varphi$   
and  $\sin \varphi$**

$\sigma_{\text{NH}_b}$  Operation

$$\cos(300^\circ - \varphi) = \cos(60^\circ + \varphi) = \frac{1}{2} \cos \varphi - \frac{\sqrt{3}}{2} \sin \varphi$$

$$\sin(300^\circ - \varphi) = -\sin(60^\circ + \varphi) = -\frac{\sqrt{3}}{2} \cos \varphi - \frac{1}{2} \sin \varphi$$

$\sigma_{\text{NH}_c}$  Operation

$$\cos(60^\circ - \varphi) = \frac{1}{2} \cos \varphi + \frac{\sqrt{3}}{2} \sin \varphi$$

$$\sin(60^\circ - \varphi) = \frac{\sqrt{3}}{2} \cos \varphi - \frac{1}{2} \sin \varphi$$

The effects on  $p_x$  orbital are shown in Table 5.7.5.

Table 5.7.5 Effects on  $p_x$  Orbital

$$E(p_x) = p_x$$

$$C_3(p_x) = C_3(\sin \theta \sin \varphi) = \sin \theta \left( -\frac{\sqrt{3}}{2} \cos \varphi - \frac{1}{2} \sin \varphi \right) = -\frac{\sqrt{3}}{2} p_y - \frac{1}{2} p_x$$

$$C_3^2(p_x) = C_3^2(\sin \theta \sin \varphi) = \sin \theta \left( \frac{\sqrt{3}}{2} \cos \varphi - \frac{1}{2} \sin \varphi \right) = \frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y$$

$$\sigma_{\text{NH}_a}(p_x) = \sigma_{\text{NH}_a}(\sin \theta \sin \varphi) = \sin \theta \sin \varphi = p_x$$

$$\sigma_{\text{NH}_b}(p_x) = \sigma_{\text{NH}_b}(\sin \theta \sin \varphi) = \sin \theta \left( -\frac{\sqrt{3}}{2} \cos \varphi - \frac{1}{2} \sin \varphi \right) = -\frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y$$

$$\sigma_{\text{NH}_c}(p_x) = \sigma_{\text{NH}_c}(\sin \theta \sin \varphi) = \sin \theta \left( \frac{\sqrt{3}}{2} \cos \varphi - \frac{1}{2} \sin \varphi \right) = \frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y$$

The effects on  $p_y$  orbital are shown in Table 5.7.6.

Table 5.7.6 Effects on  $p_y$  orbital

$$E(p_y) = p_y$$

$$C_3(p_y) = C_3(\sin \theta \sin \varphi) = \sin \theta \left( -\frac{\sqrt{3}}{2} \cos \varphi - \frac{1}{2} \sin \varphi \right) = -\frac{\sqrt{3}}{2} p_y - \frac{1}{2} p_x$$

$$C_3^2(p_y) = C_3^2(\sin \theta \sin \varphi) = \sin \theta \left( \frac{\sqrt{3}}{2} \cos \varphi - \frac{1}{2} \sin \varphi \right) = \frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y$$

$$\sigma_{\text{NH}_a}(p_y) = \sigma_{\text{NH}_a}(\sin \theta \sin \varphi) = \sin \theta \sin \varphi = p_y$$

$$\sigma_{\text{NH}_b}(p_y) = \sigma_{\text{NH}_b}(\sin \theta \sin \varphi) = \sin \theta \left( -\frac{\sqrt{3}}{2} \cos \varphi - \frac{1}{2} \sin \varphi \right) = -\frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y$$

$$\sigma_{\text{NH}_c}(p_y) = \sigma_{\text{NH}_c}(\sin \theta \sin \varphi) = \sin \theta \left( \frac{\sqrt{3}}{2} \cos \varphi - \frac{1}{2} \sin \varphi \right) = \frac{\sqrt{3}}{2} p_x - \frac{1}{2} p_y$$

**Effect on  $p_z$  Orbital**

Since  $p_z$  orbital does not involve angle  $\varphi$ , we will have

$$E(p_z) = p_z \quad C_3(p_z) = p_z \quad C_3^2(p_z) = p_z$$

$$\sigma_{\text{NH}_a}(p_z) = p_z \quad \sigma_{\text{NH}_b}(p_z) = p_z \quad \sigma_{\text{NH}_c}(p_z) = p_z$$

**Transformation Matrices**

The transformation matrices based on  $p$  orbitals for the point group  $C_{3v}$  are as follows.

$C_{3v}$	$E$	$C_3$	$C_3^2$	$\sigma_{\text{NH}_a}$	$\sigma_{\text{NH}_b}$	$\sigma_{\text{NH}_c}$	
	1	1	1	1	1	1	$p_z$
	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & -\frac{\sqrt{3}}{2} \\ \frac{2}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & \frac{\sqrt{3}}{2} \\ \frac{2}{2} & -\frac{1}{2} \end{pmatrix}$	$(p_x, p_y)$

**EXAMPLE OF d ORBITALS (PHOSPHORUS TRICHLORIDE)**

Considering the 3d orbitals of phosphorus, we have

$$d_{xy} = \sin^2 \theta \sin 2\varphi \quad d_{z^2} = 3 \cos^2 \theta - 1$$

$$d_{xz} = \sin \theta \cos \theta \cos \varphi \quad d_{x^2-y^2} = \sin^2 \theta \cos 2\varphi$$

$$d_{yz} = \sin \theta \cos \theta \sin \varphi$$

**Effect on  $\cos 2\varphi$  and  $\sin 2\varphi$** 

The effect on  $\cos 2\varphi$  and  $\sin 2\varphi$  are as follows.

 **$C_3$  Operation**

$$\cos 2(\varphi - 120^\circ) = -\cos(60^\circ - 2\varphi) = -\frac{1}{2} \cos 2\varphi - \frac{\sqrt{3}}{2} \sin 2\varphi$$

$$\sin 2(\varphi - 120^\circ) = \sin(60^\circ - 2\varphi) = \frac{\sqrt{3}}{2} \cos 2\varphi - \frac{1}{2} \sin 2\varphi$$

 **$C_3^2$  Operation**

$$\cos 2(\varphi - 240^\circ) = -\cos(60^\circ + 2\varphi) = -\frac{1}{2} \cos 2\varphi + \frac{\sqrt{3}}{2} \sin 2\varphi$$

$$\sin 2(\varphi - 240^\circ) = -\sin(60^\circ + 2\varphi) = -\frac{\sqrt{3}}{2} \cos 2\varphi - \frac{1}{2} \sin 2\varphi$$

 **$\sigma_{\text{NH}_a}$  Operation**

$$\cos 2(180^\circ - 2\varphi) = \cos 2\varphi$$

$$\sin 2(180^\circ - \varphi) = -\sin 2\varphi$$

 **$\sigma_{\text{NH}_b}$  Operation**

$$\cos 2(300^\circ - \varphi) = -\cos(60^\circ - 2\varphi) = -\frac{1}{2} \cos 2\varphi - \frac{\sqrt{3}}{2} \sin 2\varphi$$

$$\sin 2(300^\circ - \varphi) = -\sin(60^\circ - 2\varphi) = -\frac{\sqrt{3}}{2} \cos 2\varphi + \frac{1}{2} \sin 2\varphi$$

 **$\sigma_{\text{NH}_c}$  Operation**

$$\cos 2(60^\circ - \varphi) = -\cos(60^\circ - 2\varphi) = -\frac{1}{2} \cos 2\varphi + \frac{\sqrt{3}}{2} \sin 2\varphi$$

$$\sin 2(60^\circ - \varphi) = \sin(60^\circ - 2\varphi) = \frac{\sqrt{3}}{2} \cos 2\varphi + \frac{1}{2} \sin 2\varphi$$

With these, the effect on d orbitals are as follows.

Since  $d_{z^2}$  orbital does not involve angle  $\varphi$ , we will have

$$E(d_{z^2}) = d_{z^2} \quad C_3(d_{z^2}) = d_{z^2} \quad C_3^2(d_{z^2}) = d_{z^2}$$

$$\sigma_{\text{NH}_a}(d_{z^2}) = d_{z^2} \quad \sigma_{\text{NH}_b}(d_{z^2}) = d_{z^2} \quad \sigma_{\text{NH}_c}(d_{z^2}) = d_{z^2}$$

**Effect on  $d_{x^2-y^2}$  Orbital**

The effects on  $d_{x^2-y^2}$  orbital are shown in Table 5.7.5.

**Table 5.7.7 Effects on  $d_{x^2-y^2}$  orbital**

$$E(d_{x^2-y^2}) = E(\sin^2 \theta \cos 2\varphi) = \sin^2 \theta \cos 2\varphi = d_{x^2-y^2}$$

$$C_3(d_{x^2-y^2}) = C_3(\sin^2 \theta \cos 2\varphi) = \sin^2 \theta \left( -\frac{1}{2} \cos 2\varphi - \frac{\sqrt{3}}{2} \sin 2\varphi \right) = -\frac{1}{2} d_{x^2-y^2} - \frac{\sqrt{3}}{2} d_{xy}$$

$$C_3^2(d_{x^2-y^2}) = C_3^2(\sin^2 \theta \cos 2\varphi) = \sin^2 \theta \left( -\frac{1}{2} \cos 2\varphi + \frac{\sqrt{3}}{2} \sin 2\varphi \right) = -\frac{1}{2} d_{x^2-y^2} + \frac{\sqrt{3}}{2} d_{xy}$$

$$\sigma_{\text{NH}_a}(d_{x^2-y^2}) = \sigma_{\text{NH}_a}(\sin^2 \theta \cos 2\varphi) = \sin^2 \theta \cos 2\varphi = d_{x^2-y^2}$$

$$\sigma_{\text{NH}_b}(d_{x^2-y^2}) = \sigma_{\text{NH}_b}(\sin^2 \theta \cos 2\varphi) = \sin^2 \theta \left( -\frac{1}{2} \cos 2\varphi - \frac{\sqrt{3}}{2} \sin 2\varphi \right) = -\frac{1}{2} d_{x^2-y^2} - \frac{\sqrt{3}}{2} d_{xy}$$

$$\sigma_{\text{NH}_c}(d_{x^2-y^2}) = \sigma_{\text{NH}_c}(\sin^2 \theta \cos 2\varphi) = \sin^2 \theta \left( -\frac{1}{2} \cos 2\varphi + \frac{\sqrt{3}}{2} \sin 2\varphi \right) = -\frac{1}{2} d_{x^2-y^2} + \frac{\sqrt{3}}{2} d_{xy}$$

**Effect on  $d_{xy}$  Orbital**The effects on  $d_{xy}$  are shown in Table 5.7.8.**Table 5.7.8 Effects on  $d_{xy}$  orbital**

$$\begin{aligned}
 E(d_{xy}) &= E(\sin^2 \theta \sin 2\varphi) = \sin^2 \theta \sin 2\varphi = d_{xy} \\
 C_3(d_{xy}) &= C_3(\sin^2 \theta \sin 2\varphi) = \sin^2 \theta \left( \sqrt{\frac{3}{2}} \cos 2\varphi - \frac{1}{2} \sin 2\varphi \right) = \sqrt{\frac{3}{2}} d_{xz} - \frac{1}{2} d_{yz} \\
 C_3^2(d_{xy}) &= C_3^2(\sin^2 \theta \sin 2\varphi) = \sin^2 \theta \left( -\sqrt{\frac{3}{2}} \cos 2\varphi - \frac{1}{2} \sin 2\varphi \right) = -\sqrt{\frac{3}{2}} d_{xz} - \frac{1}{2} d_{yz} \\
 \sigma_{NH_3}(d_{xy}) &= \sigma_{NH_3}(\sin^2 \theta \sin 2\varphi) = -\sin^2 \theta \sin 2\varphi = -d_{xy} \\
 \sigma_{NH_6}(d_{xy}) &= \sigma_{NH_6}(\sin^2 \theta \sin 2\varphi) = \sin^2 \theta \left( -\sqrt{\frac{3}{2}} \cos \varphi + \frac{1}{2} \sin 2\varphi \right) = -\sqrt{\frac{3}{2}} d_{xz} - \frac{1}{2} d_{yz} \\
 \sigma_{NH_e}(d_{xy}) &= \sigma_{NH_e}(\sin^2 \theta \sin 2\varphi) = \sin^2 \theta \left( \sqrt{\frac{3}{2}} \cos 2\varphi + \frac{1}{2} \sin 2\varphi \right) = +\sqrt{\frac{3}{2}} d_{xz} - \frac{1}{2} d_{yz}
 \end{aligned}$$

**Effect on  $d_{xz}$  Orbital**The effects on  $d_{xz}$  are shown in Table 5.7.9.**Table 5.7.9 Effects on  $d_{xz}$  orbital**

$$\begin{aligned}
 E(d_{xz}) &= E(\sin \theta \cos \theta \sin \varphi) = \sin \theta \cos \theta \sin \varphi = d_{xz} \\
 C_3(d_{xz}) &= C_3(\sin \theta \cos \theta \sin \varphi) = \sin \theta \cos \theta \left( -\frac{1}{2} \cos \varphi + \sqrt{\frac{3}{2}} \sin \varphi \right) = -\frac{1}{2} d_{xz} + \sqrt{\frac{3}{2}} d_{yz} \\
 C_3^2(d_{xz}) &= C_3^2(\sin \theta \cos \theta \sin \varphi) = \sin \theta \cos \theta \left( \frac{1}{2} \cos \varphi - \sqrt{\frac{3}{2}} \sin \varphi \right) = -\frac{1}{2} d_{xz} - \sqrt{\frac{3}{2}} d_{yz} \\
 \sigma_{NH_3}(d_{xz}) &= \sigma_{NH_3}(\sin \theta \cos \theta \sin \varphi) = -\sin \theta \cos \theta \sin \varphi = -d_{xz} \\
 \sigma_{NH_6}(d_{xz}) &= \sigma_{NH_6}(\sin \theta \cos \theta \sin \varphi) = +\sin \theta \cos \theta \left( \frac{1}{2} \cos \varphi - \sqrt{\frac{3}{2}} \sin \varphi \right) = \frac{1}{2} d_{xz} - \sqrt{\frac{3}{2}} d_{yz} \\
 \sigma_{NH_e}(d_{xz}) &= \sigma_{NH_e}(\sin \theta \cos \theta \sin \varphi) = \sin \theta \cos \theta \left( \frac{1}{2} \cos \varphi + \sqrt{\frac{3}{2}} \sin \varphi \right) = \frac{1}{2} d_{xz} + \sqrt{\frac{3}{2}} d_{yz}
 \end{aligned}$$

**Effect on  $d_{yz}$  Orbital**The effects on  $d_{yz}$  are shown in Fig. 5.7.10.**Table 5.7.10 Effects on  $d_{yz}$  orbital**

$$\begin{aligned}
 E(d_{yz}) &= E(\sin \theta \cos \theta \sin \varphi) = \sin \theta \cos \theta \sin \varphi = d_{yz} \\
 C_3(d_{yz}) &= C_3(\sin \theta \cos \theta \sin \varphi) = \sin \theta \cos \theta \left( -\sqrt{\frac{3}{2}} \cos \varphi - \frac{1}{2} \sin \varphi \right) = -\sqrt{\frac{3}{2}} d_{xz} - \frac{1}{2} d_{yz} \\
 C_3^2(d_{yz}) &= C_3^2(\sin \theta \cos \theta \sin \varphi) = \sin \theta \cos \theta \left( \sqrt{\frac{3}{2}} \cos \varphi - \frac{1}{2} \sin \varphi \right) = \sqrt{\frac{3}{2}} d_{xz} - \frac{1}{2} d_{yz} \\
 \sigma_{NH_3}(d_{yz}) &= \sigma_{NH_3}(\sin \theta \cos \theta \sin \varphi) = \sin \theta \cos \theta \sin \varphi = d_{yz} \\
 \sigma_{NH_6}(d_{yz}) &= \sigma_{NH_6}(\sin \theta \cos \theta \sin \varphi) = \sin \theta \cos \theta \left( -\sqrt{\frac{3}{2}} \cos \varphi - \frac{1}{2} \sin \varphi \right) = -\sqrt{\frac{3}{2}} d_{xz} - \frac{1}{2} d_{yz} \\
 \sigma_{NH_e}(d_{yz}) &= \sigma_{NH_e}(\sin \theta \cos \theta \sin \varphi) = \sin \theta \cos \theta \left( \sqrt{\frac{3}{2}} \cos \varphi - \frac{1}{2} \sin \varphi \right) = \sqrt{\frac{3}{2}} d_{xz} - \frac{1}{2} d_{yz}
 \end{aligned}$$

**Transformation Matrices**The transformation matrices based on d orbitals for the point group  $C_{3v}$  are as follows.

$C_{3v}$	$E$	$C_3$	$C_3^2$	$\sigma_{NH_3}$	$\sigma_{NH_6}$	$\sigma_{NH_e}$	
1	1	1	1	1	1	1	$d_z$
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & -\sqrt{3} \\ -\frac{2}{\sqrt{3}} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & \sqrt{3} \\ \frac{2}{\sqrt{3}} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & -\sqrt{3} \\ -\frac{2}{\sqrt{3}} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & \sqrt{3} \\ \frac{2}{\sqrt{3}} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & \sqrt{3} \\ -\frac{2}{\sqrt{3}} & \frac{1}{2} \end{pmatrix}$	$(d_{x^2-y^2}, d_{xy})$
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & \sqrt{3} \\ -\frac{2}{\sqrt{3}} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & -\sqrt{3} \\ \frac{2}{\sqrt{3}} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & \sqrt{3} \\ -\frac{2}{\sqrt{3}} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & -\sqrt{3} \\ \frac{2}{\sqrt{3}} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & \sqrt{3} \\ -\frac{2}{\sqrt{3}} & \frac{1}{2} \end{pmatrix}$	$(d_{xz}, d_{yz})$

**5.8 REDUCIBLE AND IRREDUCIBLE REPRESENTATIONS**

Section 5.7 describes a few bases of representations of symmetry operations of a point group. In this section, we consider their classification in terms of reducible and irreducible representations.

The  $C_{3v}$  representation of the point group  $C_{3v}$ , based on the bond vectors of  $NH_3$  molecule is

$$A = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

Let this matrix be subjected to a similarity transformation  $X^{-1}AX$  where the matrix  $X$  is given by

$$X = \begin{pmatrix} -2/3x & 0 & -1/3y \\ 1/3x & -1/\sqrt{3}x & -1/3y \\ -1/3x & 1/\sqrt{3}x & -1/3y \end{pmatrix}$$

where  $x = \sqrt{2/3}$  and  $y = \sqrt{1/3}$ . The matrix  $X^{-1}$  is the inverse of matrix  $X$  (by definition,  $XX^{-1} = E$ ) and is given by

$$X^{-1} = \begin{pmatrix} -x & x/2 & x/2 \\ 0 & -\sqrt{3}x/2 & \sqrt{3}x/2 \\ -y & -y & -y \end{pmatrix}$$

Thus

$$AX = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} -2/3x & 0 & -1/3y \\ 1/3x & -1/\sqrt{3}x & -1/3y \\ 1/3x & 1/\sqrt{3}x & -1/3y \end{pmatrix} = \begin{pmatrix} 1/3x & 1/\sqrt{3}x & -1/3y \\ -2/3x & 0 & -1/3y \\ -1/3x & -1/\sqrt{3}x & -1/3y \end{pmatrix}$$

$$S = X^{-1}(AX) = \begin{pmatrix} -x & x/2 & x/2 \\ 0 & -\sqrt{3}x/2 & \sqrt{3}x/2 \\ -y & -y & -y \end{pmatrix} \begin{pmatrix} 1/3x & 1/\sqrt{3}x & -1/3y \\ -2/3x & 0 & -1/3y \\ 1/3x & -1/\sqrt{3}x & -1/3y \end{pmatrix} \\ = \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

We find that the matrix  $A$  (which involves zeros along the diagonal and at the other places distributed unsymmetrically about the diagonal) is transformed into the matrix  $S$  (which involves zeros distributed symmetrically about the diagonal). Moreover, the nonzero elements in the matrix  $S$  are distributed along the diagonal into two blocks of the order  $2 \times 2$  and  $1 \times 1$ , respectively.

If now the above similarity transformation involving the same matrices  $X$  and  $X^{-1}$  is extended to the corresponding matrices of the remaining symmetry operations of the point group  $C_{3v}$ , we get

$$X^{-1}C_3^2X = X^{-1} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} X = \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \equiv \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \quad \text{and} \quad (1)$$

$$X^{-1}\sigma_v(1)X = X^{-1} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} X = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \text{and} \quad (1)$$

$$X^{-1}\sigma_v(2)X = X^{-1} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} X = \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \equiv \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix} \quad \text{and} \quad (1)$$

$$X^{-1}\sigma_v(3)X = X^{-1} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} X = \begin{pmatrix} -1/2 & \sqrt{3}/2 & 3 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \equiv \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix} \quad \text{and} \quad (1)$$

We find that each of the original matrix representation is changed into a matrix involving nonzero elements along the diagonal and each one is factored into two identically situated  $2 \times 2$  and  $1 \times 1$  blocks, respectively. We also find that the resultant matrices are identical to the matrix representations based on the translational vectors  $T_x$  and  $T_y$  (taken together) and  $T_z$ , respectively. Thus, the above similarity transformation is equivalent to changing the basis of representation from bond vectors to translational vectors.

Since the matrix  $A$  can be converted into two matrices of the lower orders by a suitable similarity transformation, the representation depicted by the matrix  $A$  is said to be reducible representation. If the resultant matrices cannot be reduced further by a similarity transformation, the corresponding representation is said to represent irreducible representation.

The irreducible representations play fundamental role in the application of symmetry to molecular problems.

## 5.9 CHARACTERS OF MATRICES

By definition, character (symbol:  $\chi$ ) of a square matrix of dimension  $n$  is the sum of its diagonal elements, i.e.

$$\chi = \sum_{i=1}^n a_{ii} \quad (5.9.1)$$

It is found that the informations conveyed by the transformation matrices of any representation is contained in the character of these matrices.

There are two theorems concerning the behaviour of characters. These are as follows.

If  $C = AB$  and  $D = BA$ , then the characters of  $C$  and  $D$  are identical.

By definition,

$$\text{Character of } C = \sum_{i=1}^n C_{ii} = \sum_{i=1}^n \left( \sum_{k=1}^n a_{ik} b_{ki} \right)$$

$$= \sum_{i=1}^n \left( \sum_{k=1}^n b_{ki} a_{ik} \right) \quad (\text{Product of two numbers is commutative})$$

$$= \sum_{k=1}^n \left( \sum_{i=1}^n b_{ki} a_{ik} \right) \quad (\text{Order of summation is immaterial})$$

$$= \sum_{k=1}^n d_{kk} = \text{Character of } D \quad (5.9.2)$$

**Theorem 2**

Conjugate matrices have identical characters.

The conjugate matrices  $A$  and  $B$  are related to each other by the expression

$$B = X^{-1}AX$$

where  $X$  is a square matrix such that the product of  $X^{-1}$  and  $X$  yields a unit matrix  $E$ , i.e.  $X^{-1}X = E$ . Let us represent  $C = AX$  and  $Y = X^{-1}$ . Hence  $B = YC$ . Now

$$\begin{aligned} \text{Character of } B &= \sum_{i=1}^n b_{ii} = \sum_{i=1}^n \left( \sum_{k=1}^n y_{ik} c_{ki} \right) = \sum_{i=1}^n \sum_{k=1}^n y_{ik} \left( \sum_{j=1}^n a_{kj} x_{ji} \right) \\ &= \sum_{i=1}^n \sum_{k=1}^n \sum_{j=1}^n y_{ik} a_{kj} x_{ji} = \sum_{k=1}^n \sum_{j=1}^n a_{kj} \left( \sum_{i=1}^n y_{ik} x_{ji} \right) \\ &= \sum_{k=1}^n \sum_{j=1}^n a_{kj} e_{jk} \end{aligned} \quad (5.9.3)$$

Since  $E$  is a unit matrix, we will have

$$\delta_{jk} = 1 \text{ when } j = k$$

$$\delta_{jk} = 0 \text{ when } j \neq k$$

$$e_{jk} = \delta_{jk}$$

With this, we can write the above expression as

$$\text{Character of } B = \sum_{k=1}^n a_{kk} = \text{character of } A \quad (5.9.5)$$

Since reducible representation and irreducible representation are related to each other through similarity transformation, their characters are identical.

**5.10 THE GREAT ORTHOGONALITY THEOREM**

The elements of the matrices which constitute the irreducible representations of a group follow 'the great orthogonality theorem' which is stated as follows.

$$\sum_R [\Gamma_i(R)_{mn}][\Gamma_j(R)_{m'n'}]^* = \frac{h}{\sqrt{I_i I_j}} \delta_{ij} \delta_{mm'} \delta_{nn'} \quad (5.10.1)$$

where

- (i) The summation  $R$  represents the summation of various operations in a group.
- (ii)  $\Gamma_i(R)_{mn}$  represents the matrix element  $R_{mn}$  of the matrix  $R$  representing  $R$ th symmetry operation of the  $i$ th representation of a group.
- (iii)  $[\Gamma_j(R)_{m'n'}]^*$  represents the complex conjugate of the matrix element  $R_{m'n'}$  of the matrix  $R$  representing  $R$ th symmetry operation of the  $j$ th representation of a group.

(iv)  $h$  is the order of a group which is equal to the number of symmetry operations in a group.

(v)  $I_i$  and  $I_j$  are the dimensions of the  $i$ th and  $j$ th representations (which respectively are equal to the order of the corresponding matrices) of a group.

(vi)  $\delta_{ij}$  stands for Kronecker delta. Its value is 1 if  $i = j$ , and is zero if  $i \neq j$ .

In the simpler forms, Eq. (5.10.1) may be written as

$$(i) \quad \sum_R \Gamma_i(R)_{mn} \Gamma_j(R)_{mn} = 0 \text{ if } i \neq j$$

This implies that the sum of the products of the corresponding elements of matrices of the various symmetry operations belonging to two different irreducible representations is zero.

**Illustration** The irreducible representations of water based on the translational vectors are

$C_{2v}$	$E$	$C_2$	$\sigma(xz)$	$\sigma(yz)$	
$\Gamma_x$	+1	-1	+1	-1	$T_x$
$\Gamma_y$	+1	-1	-1	+1	$T_y$
$\Gamma_z$	+1	+1	+1	+1	$T_z$

Taking  $\Gamma_x$  and  $\Gamma_y$  representations, we have

$$\begin{aligned} &\Gamma_x(E) \Gamma_y(E) + \Gamma_x(C_2) \Gamma_y(C_2) + \Gamma_x(\sigma_{xz}) \Gamma_y(\sigma_{xz}) + \Gamma_x(\sigma_{yz}) \Gamma_y(\sigma_{yz}) \\ &= (+1)(+1) + (-1)(-1) + (+1)(-1) + (-1)(+1) = 0 \end{aligned}$$

Similarly, it can be shown that sum is zero for each of the two representations ( $\Gamma_x$  and  $\Gamma_z$ ), and ( $\Gamma_y$  and  $\Gamma_z$ ).

$$(ii) \quad \sum_R \Gamma_i(R)_{mn} \Gamma_j(R)_{m'n'} = 0 \text{ if } m \neq m' \text{ and/or } n \neq n'.$$

This implies that the sum of the products of two corresponding different elements of matrices of the various symmetry operations belonging to the same irreducible representation is zero.

**Illustration** The irreducible representation of the point group  $C_{3v}$  based on the translational vectors ( $T_x$  and  $T_y$ ) is

$C_{3v}$	$E$	$C_3^1$	$C_3^2$	$\sigma_v'$	$\sigma_v''$	$\sigma_v'''$	
	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} T_x \\ T_y \end{pmatrix}$

Taking matrix elements (1, 1) and (1, 2), we have

$$\begin{aligned} E(1, 1)E(1, 2) + C_3^1(1, 1)C_3^1(1, 2) + C_3^2(1, 1)C_3^2(1, 2) + \\ \alpha_4'(1, 1)\alpha_4'(1, 2) + \alpha_4''(1, 1)\alpha_4''(1, 2) + \alpha_4'''(1, 1)\alpha_4'''(1, 2) \\ = 1 \times 0 + (-1/2)(-\sqrt{3}/2) + (-1/2)(\sqrt{3}/2) + 1 \times 0 + (-1/2)(-\sqrt{3}/2) \\ + (-1/2)(\sqrt{3}/2) = 0 \end{aligned}$$

Similarly working for other pairs (1, 1) and (2, 1), and (1, 1) and (2, 2), and (2, 1) and (2, 2), we find that the sum is zero for each of them.

$$(iii) \quad \sum_R \Gamma_i(R)_{mn} \Gamma_j(R)_{mn} = h/I_i$$

This implies that the sum of square of the corresponding element of matrices of the various symmetry operations belonging to the same irreducible representation is equal to order of the point group divided by the dimension of matrices of the irreducible representation.

**Illustration** Taking the element (1, 1) of the matrices of irreducible representations of the point group  $C_{3v}$ , we find that

$$\begin{aligned} \{E(1, 1)\}^2 + \{C_3^1(1, 1)\}^2 + \{C_3^2(1, 1)\}^2 + \{\alpha_4'(1, 1)\}^2 + \{\alpha_4''(1, 1)\}^2 \\ + \{\alpha_4'''(1, 1)\}^2 = h/I \end{aligned}$$

$$\text{i.e.} \quad 1^2 + (-1/2)^2 + (-1/2)^2 + 1^2 + (-1/2)^2 + (-1/2)^2 = 3 = 6/2$$

Similarly working for other elements (1, 2), (2, 1) and (2, 2), we find that each is equal to 3.

## 5.11 CHARACTERISTICS OF IRREDUCIBLE REPRESENTATIONS

**Rule 1** The following characteristics hold good for irreducible representations.

*The sum of the squares of characters of identity operations of the irreducible representations of a group is equal to the order of the group, that is*

$$\sum_i [\chi_i(E)]^2 = h \quad (5.11.1)$$

The irreducible representation of an identity operation involves +1 in one-dimensional representation or +1 along the diagonal of its matrix representation. Thus, the character of identity operation will be equal to the order of its representation. Hence, this rule may be stated as follows.

The sum of squares of the dimensions of the irreducible representations of a group is equal to the order of the group, that is

$$\sum_i I_i^2 = h \quad (5.11.2)$$

The sum of the squares of the characters of symmetry operations in any irreducible representations equals  $h$ , that is

$$\sum_R [\chi_i(R)]^2 = h_i \quad (5.11.3)$$

**Rule 2**

**Rule 3**

**Explanation** This rule follows from 'The Great Orthogonality Theorem':

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_j(R)_{m'n'}] = \frac{h}{\sqrt{I_i I_j}} \delta_{ij} \delta_{mm'} \delta_{nn'} \quad (\text{Eq. 5.11.1})$$

For the same representation  $i = j$

For the diagonal elements  $m = n$  and  $m' = n'$

For the above conditions, Eq. (5.11.1) is reduced to

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_i(R)_{m'n'}] = \frac{h}{I_i} \delta_{mm'}$$

Carrying out the summation over  $m$  and  $m'$  gives

$$\sum_R \left[ \sum_m \Gamma_i(R)_{mn} \right] \left[ \sum_{m'} \Gamma_i(R)_{m'n'} \right] = \frac{h}{I_i} \left( \sum_m \sum_{m'} \delta_{mm'} \right)$$

$$\text{or} \quad \sum_R \chi_i(R) \chi_i(R) = \frac{h}{I_i} I_i$$

$$\text{or} \quad \sum_R [\chi_i(R)]^2 = h_i$$

The sum of products of corresponding characters of two different irreducible representations is equal to zero, that is

$$\sum_R \chi_i(R) \chi_j(R) = 0 \text{ when } i \neq j. \quad (5.11.4)$$

**Explanation** This rule follows from 'The Great Orthogonality Theorem'.

For two different representations  $i \neq j$ .

For the corresponding elements in two different representations

$$m = m' \text{ and } n = n'$$

For the diagonal elements  $m = n$  and  $m' = n'$ .

For these facts, Eq. (5.11.1) is reduced to

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_j(R)_{mn}] = 0 \text{ for } i \neq j.$$

Carrying summation of  $m$  for the two representations, we get

$$\sum_R \left[ \sum_m \Gamma_i(R)_{mn} \right] \left[ \sum_m \Gamma_j(R)_{mn} \right] = 0 \text{ for } i \neq j.$$

$$\sum_R \chi_i(R) \chi_j(R) = 0 \text{ for } i \neq j.$$

**Note:** Rules 2 and 3 can be written together by the expression

$$\sum_R \chi_i(R) \chi_j(R) = h_i \delta_{ij} \quad (5.11.5)$$

In a given representation (reducible or irreducible) the characters of all matrices belonging to the symmetry operations in the same class are identical.

**Rule 4**



**Explanation** This follows from the fact that the representations of the operations in the same class are conjugate to one another through similarity transformations. Moreover, the characters of the representations remain unaltered in a similarity transformation.

The number of irreducible representations of a group is equal to the number of classes in the group.

### Rule 5

## 5.12 WORKED OUT EXAMPLES OF IRREDUCIBLE REPRESENTATIONS OF A GROUP

### Irreducible Representations of the Point Group $C_{2v}$

The group  $C_{2v}$  includes four symmetry operations, namely,  $E$ ,  $C_2$ ,  $\sigma(xz)$  and  $\sigma(yz)$ , and each one constitutes a separate class.

According to Rule 5, the group  $C_{2v}$  will have four irreducible representations.

According to Rule 1, we will have

$$\sum_i I_i^2 = h \quad (\text{Eq. 5.11.1})$$

Since  $h = 4$ , we have

$$I_1^2 + I_2^2 + I_3^2 + I_4^2 = 4$$

Obviously, we will have

$$I_1 = I_2 = I_3 = I_4 = 1$$

that is, each of the four irreducible representations of the point group  $C_{2v}$  is one-dimensional.

Rule 2 states that

$$\sum_R [\chi_i(R)]^2 = h \quad (\text{Eq. 5.11.3})$$

Hence, the characters of representations in any one irreducible representation will be either equal to +1 or -1, i.e.

$$\chi_i(R) = \pm 1.$$

Let one of the representations has  $\chi(R) = +1$  for each operation  $R$ , i.e.

	$E$	$C_2$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_1$	1	1	1	1

Rule 3 states that

$$\sum_R \chi_i(R)\chi_j(R) = 0 \quad (\text{Eq. 5.11.4})$$

This implies that each of the remaining three irreducible operations has two +1's and two -1's as the characters. Since the character of identity operation is always +1, we have to distribute one +1 and two -1's in the remaining three operations, namely,  $C_2$ ,  $\sigma(xz)$  and  $\sigma(yz)$ . Hence, we will have

$C_{2v}$	$E$	$C_2$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_1$	1	1	1	1
$\Gamma_2$	1	1	-1	-1
$\Gamma_3$	1	-1	1	-1
$\Gamma_4$	1	-1	-1	1

### Irreducible Representations of the Point Group $C_{3v}$

Equation (5.11.4) is satisfied for any two irreducible representations listed above. This is often stated as that the two irreducible representations of a group are orthogonal to each other.

- The elements of the point group  $C_{3v}$  are  $E$ ,  $C_3$ ,  $C_3^2$ ,  $\sigma_v(1)$ ,  $\sigma_v(2)$  and  $\sigma_v(3)$ . These belong to three classes, elements of which are  $E$ ,  $2C_3$  and  $3\sigma_v$ .
- Rule 5 states that the point group  $C_{3v}$  will have three irreducible representations.
- Rule 1 states that

$$I_1^2 + I_2^2 + I_3^2 = h = 6$$

The only possibility satisfying the above expression is 1, 1 and 2, i.e. there are two one-dimensional representations and one two-dimensional representation.

Rule 2 states that

$$\sum_R [\chi_i(R)]^2 = h$$

One of the irreducible representations will have +1 as the character for each of six symmetry operations, i.e.

	$E$	$2C_3$	$3\sigma_v$
$\Gamma_1$	1	1	1

$$\text{such that } [\chi(E)]^2 + 2[\chi(C_3)]^2 + 3[\chi(\sigma_v)]^2 = 1^2 + 2 \times 1^2 + 3 \times 1^2 = 6$$

Rule 3 states that

$$\sum_R \chi_i(R)\chi_j(R) = 0 \quad \text{when } i \neq j$$

We are looking for two other representations, each one of which is orthogonal to the representation  $\Gamma_1$  listed above. One of the possibilities that there are three +1's and three -1's as the characters. Since all the symmetry operations in a class has the same character, we will have

	$E$	$2C_3$	$3\sigma_v$
$\Gamma_2$	1	1	-1

- We are left with only one more representation of dimension 2. Since the matrix corresponding to identity operation has +1 in each of its diagonal elements, we will have

$$\chi(E) = 2$$

- The characters of the classes  $C_3$  and  $\sigma_v$  can be worked out by using Rule 3

$$\left( \sum_R \chi_i(R)\chi_j(R) = 0 \right).$$

For the representations 1 and 3, we get

$$\chi_1(E)\chi_3(E) + 2\chi_1(C_3)\chi_3(C_3) + 3\chi_1(\sigma_v)\chi_3(\sigma_v) = 0$$

$$\text{i.e. } (1)(2) + 2(1)\chi_3(C_3) + 3(1)\chi_3(\sigma_v) = 0 \quad (5.12.1)$$

For the representations 2 and 3, we get

$$\chi_2(E)\chi_3(E) + 2\chi_2(C_3)\chi_3(C_3) + 3\chi_2(\sigma)\chi_3(\sigma) = 0$$

$$\text{i.e. } (1)(2) + 2(1)\chi_3(C_3) + 3(-1)\chi_3(\sigma) = 0 \quad (5.12.2)$$

Equations (5.12.1) and (5.12.2) may be solved for  $\chi_3(C_3)$  and  $\chi_3(\sigma)$ , which gives

$$\chi_3(C_3) = -1 \quad \text{and} \quad \chi_3(\sigma) = 0$$

Thus, the third representation is

	E	$2C_3$	$3\sigma_v$
$\Gamma_3$	2	-1	0

The complete set of characters of irreducible representations of the group  $C_{3v}$  is

$C_{3v}$	E	$2C_3$	$3\sigma_v$
$\Gamma_1$	1	1	1
$\Gamma_2$	1	1	-1
$\Gamma_3$	2	-1	0

### 5.13 RESOLUTION OF A REDUCIBLE REPRESENTATION IN TERMS OF IRREDUCIBLE REPRESENTATIONS

As described earlier, a reducible representation of a group can be converted into irreducible representations by a suitable similarity transformation. However, without going into such a mathematical exercise, it is possible to determine nature and number of irreducible representations by using the expression

$$a_i = \frac{1}{h_i} \sum_R \chi(R)\chi_i(R) \quad (5.13.1)$$

where  $a_i$  is the number of times the  $i$ th irreducible representation present in the reducible representation. The summation is carried over all the symmetry operations of the group of order  $h$  and  $\chi(R)$  and  $\chi_i(R)$  are the characters of the operation  $R$  in reducible and irreducible representations, respectively.

Since the character of a matrix is not changed during a similarity transformation, we can write

$$\chi(R) = \sum_j a_j \chi_j(R) \quad (5.13.2)$$

where  $\chi(R)$  is the character of the matrix corresponding to operation  $R$  in the reducible representation, and  $a_j$  is the number of times the  $j$ th irreducible representation appear in the reducible matrix of operation  $R$  and  $\chi_j(R)$  is the character of the matrix corresponding to operation in the  $j$ th irreducible representation.

Multiplying Eq. (5.13.2) by  $\chi_i(R)$  and carrying out the summation over  $R$ 's of the group, we get

#### Illustration

$$\sum_R \chi(R)\chi_i(R) = \sum_j a_j \left\{ \sum_R \chi_i(R)\chi_j(R) \right\}$$

$$= \sum_j a_j h_i \delta_{ij} \quad (\text{using Eq. 5.11.5})$$

$$= a_i h_i \quad (\text{only the term having } i = j \text{ survives})$$

$$\text{Hence } a_i = \frac{1}{h_i} \sum_R \chi(R)\chi_i(R)$$

Since the characters of operations within a class are identical, we can write the above expression as

$$a_i = \frac{1}{h_i} \sum_C n_C \chi(C)\chi_i(C) \quad (5.13.3)$$

where the summation is over the classes of a group.

One of the reducible representations of  $H_2O$  molecule obtained by placing three vectors on each atom along the Cartesian axes with atom as an origin (see, Section 5.16) is

$C_{2v}$	E	$C_2$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{3v}$	9	-1	1	3

We can work out the nature and number of irreducible representations in the above reducible representation by using Eq. (5.13.1). The irreducible representations of the point group  $C_{2v}$  are

$C_{2v}$	E	$C_2$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_1$	1	1	1	1
$\Gamma_2$	1	1	-1	-1
$\Gamma_3$	1	-1	1	-1
$\Gamma_4$	1	-1	-1	1

#### Numbers of representations

$$a_1 = \frac{1}{4} [ \chi(E)\chi_1(E) + \chi(C_2)\chi_1(C_2) + \chi(\sigma_{xz})\chi_1(\sigma_{xz}) + \chi(\sigma_{yz})\chi_1(\sigma_{yz}) ]$$

$$= \frac{1}{4} [ 9 \times 1 + (-1)(1) + (1)(1) + (3)(1) ] = 3$$

$$a_2 = \frac{1}{4} [ 9 \times 1 + (-1)(1) + (1)(-1) + (3)(-1) ] = 1$$

$$a_3 = \frac{1}{4} [ 9 \times 1 + (-1)(-1) + (1)(1) + (3)(-1) ] = 2$$

$$a_4 = \frac{1}{4} [ 9 \times 1 + (-1)(-1) + (1)(-1) + (3)(1) ] = 3$$

Hence, the occurrence of  $\Gamma_1$ ,  $\Gamma_2$ ,  $\Gamma_3$  and  $\Gamma_4$  in the reducible representation  $\Gamma_{3v}$  are 3, 1, 2 and 3, respectively. We can verify the above conclusion by writing explicitly these configurations as shown in the following.

$C_{2v}$	$E$	$C_2$	$\sigma(xz)$	$\sigma(yz)$
Three times $\Gamma_1$	3(1)	3(1)	3(1)	3(1)
One time $\Gamma_2$	1(1)	1(1)	1(-1)	1(-1)
Two times $\Gamma_3$	2(1)	2(-1)	2(1)	2(-1)
Three times $\Gamma_4$	3(1)	3(-1)	3(-1)	3(1)
Sum	9	-1	1	3

### 5.14 DESCRIPTION OF A CHARACTER TABLE

A character table lists all irreducible representations of a group. The general layout of such a table is as follows

I	II	IV	V	VI
III				

where the sections I to VI are as follows.

**Section I** This place lists the Schönflies symbol of the point group.

**Section II** This place lists the classwise symmetry operations of the point group.

**Section III** This place lists the Mulliken's symbols of the irreducible representations. These are described in Section 5.15.

**Section IV** This place lists row-wise the characters of symmetry operations (classwise) against the irreducible representations listed in Section III.

**Section V** This place lists the translational vectors ( $x, y, z$ ) and rotational vectors ( $R_x, R_y, R_z$ ) which form the bases of irreducible representations.

**Section VI** This place provides information about the binary combinations of  $x, y$  and  $z$  which form the bases of certain irreducible representations.

### 5.15 DESCRIPTION OF MULLIKEN SYMBOLS

- A one-dimensional representation is designated as A if the character of rotation about the principal axis (rotation axis of highest order) is +1.  
If the character is -1, the representation is designated as B.
- The symbol A or B is subscripted by '1' if the character of rotation about  $C_2$  axis perpendicular to the principal axis is +1. If  $C_2$  axis does not exist, the character of reflection in a  $\sigma_v$  plane should be +1.  
If the character is -1, the symbol A or B carries the subscript '2'.
- If there exists a centre of symmetry, the subscript '1' or '2' is appended with 'g' (from gerade) if the character of inversion operation is +1. It is appended with 'u' (from ungerade) if the character of inversion is -1.
- The symbol A or B is superscripted by a single prime (') if the character of reflection in a  $\sigma_h$  plane is +1. If it is -1, the symbol is superscripted by a double prime ('').

- Designation of higher-dimensional representation goes as follows.  
Two-dimensional by E  
Three-dimensional by T or F  
Four-dimensional by G  
Five-dimensional by H, and so on.
- A different notation is usually used for the linear groups  $C_{\infty v}$  and  $D_{\infty h}$ . The symbols used here are  $\Sigma, \Pi, \Delta, \Phi$ , etc., depending upon the unit 0,  $\pm 1, \pm 2, \pm 3$ , etc., respectively, of angular momentum component about the linear axis. Such a symbolism corresponds to the s, p, d, f notation for the azimuthal quantum number  $l$  for atoms.

The above symbols are used to represent the symmetry behaviour of normal modes, molecular orbitals, and electronic and vibrational wave functions.

### 5.16 REDUCIBLE REPRESENTATION BASED ON TRANSLATIONAL VECTORS AND ITS RESOLUTION INTO IRREDUCIBLE REPRESENTATIONS—REVISITED

In this section, we consider an important reducible representation which is useful in the study of molecular structure.

Taken each atom as the origin, we can position three vectors along the Cartesian coordinates. For water molecule, it is shown in Fig. 5.16.1.

#### Three Mutually Perpendicular Vectors on Each Atom

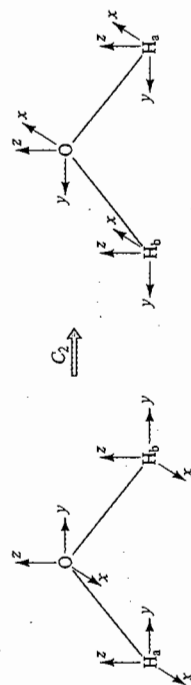


Fig. 5.16.1 Three mutually perpendicular vectors on each atom of  $H_2O$

The operation  $C_2$  causes the following changes.

$$\begin{aligned} x'(H_a) &= -x(H_b) & x'(H_b) &= -x(H_a) & x'(O) &= -x(O) \\ y'(H_a) &= -y(H_b) & y'(H_b) &= -y(H_a) & y'(O) &= -y(O) \\ z'(H_a) &= z(H_b) & z'(H_b) &= z(H_a) & z'(O) &= z(O) \end{aligned}$$

The matrix representation of the above changes is

$$\begin{bmatrix} x'(H_a) \\ y'(H_a) \\ z'(H_a) \\ x'(H_b) \\ y'(H_b) \\ z'(H_b) \\ x'(O) \\ y'(O) \\ z'(O) \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x(H_a) \\ y(H_a) \\ z(H_a) \\ x(H_b) \\ y(H_b) \\ z(H_b) \\ x(O) \\ y(O) \\ z(O) \end{bmatrix}$$

new coordinates      transformation matrix      original coordinates

The character of the above transformation matrix is  $-1$ .

Instead of writing explicitly the transformation matrix of each operation, one can determine its character by the following observations.

- If an atom and its associated vectors are shifted to a different position in space by any symmetry operation, then the corresponding diagonal positions include only zeros and thus their contributions towards the character of the transformation matrix is zero.
- If an atom remains unshifted in a symmetry operation, the corresponding diagonal positions include nonzeros and their contributions towards the character of the transformation matrix is nonzero.

Thus, the working procedure to determine the character of transformation of an operation (one in each class is sufficient) is to count the number of unshifted atoms and determine the corresponding affects on the vectors following the rules given below.

We now list the guidelines to determine character for a given symmetry operation on a molecule

**Identity Operation** All atoms and also their vectors remain unshifted. For each atom, there will be  $+1$  for each of the three vectors along the diagonal of the transformation matrix and hence its contribution towards character is  $+3$  for each atom.

**Inversion Operation** The effect of inversion is the reversal of direction of vectors on each atom. Hence, for each unshifted atom, the contribution towards the character is  $-1$  for each vector and a total of  $-3$  for all the three vectors.

**Reflection Operation** The effect of reflection is the reversal of direction of the vector perpendicular to the reflection plane. The directions of other two vectors remain unaltered. Hence, the contribution per atom towards character is  $+1$  ( $= +1 + 1 - 1$ ).

**Rotation Operation** The effect of clockwise rotation about the  $z$ -axis by an angle  $\theta$  is expressed as

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Hence, the contribution towards character of an unshifted atom is  $1 + 2 \cos \theta$ .

**Improper Rotation** The effect of clockwise rotation about the  $z$ -axis followed by reflection in a plane perpendicular to  $z$ -axis is expressed as

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Hence, the contribution towards character of an unshifted atom is  $-1 + 2 \cos \theta$ .

With the above guidelines, we can tabulate the reducible representation of a group.

### Example of Water

For water (point group  $C_{2v}$ ), we have

$C_{2v}$	$E$	$C_2$	$\sigma_x$	$\sigma_y$
Unshifted atom $\Gamma_{3N}$	3 (all the three atoms)	1 (oxygen atom)	1 (oxygen atom)	3 (all the three atoms)
	$3(+3) = 9$	$1(1 + 2 \cos 180^\circ) = -1$	$1(+1) = +1$	$3(+1) = +3$

### Example of $NH_3$

For  $NH_3$  (point group  $C_{3v}$ ), we have

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$
Unshifted atoms $\Gamma_{3N}$	4 (all the four atoms)	1 (nitrogen atom)	2 (nitrogen atom and one of H atoms)
	$4(+3) = 12$	$1(1 + 2 \cos 120^\circ) = 0$	$2(+1) = +2$

### Reduction into

Once we know reducible representation of a group, we can find out the irreducible representations contained in it by using the expression

$$a_i = \frac{1}{h_i} \sum_C n_C \chi(C) \chi_i(C) \quad (\text{Eq. 5.13.3})$$

For  $H_2O$  (point group  $C_{2v}$ ), we have

### Irreducible Representations of Water

Reducible representation	$E$	$C_2$	$\sigma_x$	$\sigma_y$
$\Gamma_{3N}$	9	-1	1	3
	$A_1$	1	1	1
	$A_2$	1	1	-1
	$B_1$	1	-1	1
	$B_2$	1	-1	-1

$$a(A_1) = \frac{1}{4} [1(9)(1) + 1(-1)(1) + 1(1)(1) + 1(3)(1)] = 3$$

$$a(A_2) = \frac{1}{4} [1(9)(1) + 1(-1)(1) + 1(1)(-1) + 1(3)(-1)] = 1$$

$$a(B_1) = \frac{1}{4} [1(9)(1) + 1(-1)(-1) + 1(1)(1) + 1(3)(-1)] = 2$$

$$a(B_2) = \frac{1}{4} [1(9)(1) + 1(-1)(-1) + 1(1)(-1) + 1(3)(1)] = 3$$

$$\text{Hence } \Gamma_{3N} = 3A_1 + A_2 + 2B_1 + 3B_2 \quad (5.16.1)$$

For  $NH_3$  (point group  $C_{3v}$ ), we have

Reducible representation	$E$	$2C_3$	$3\sigma_v$
Unshifted atoms $\Gamma_{3N}$	4	1	2
	$A_1$	1	1
	$A_2$	1	-1
	$E$	2	-1

$$a(A_1) = \frac{1}{6} [(1)(12)(1) + (2)(0)(1) + 3(2)(1)] = 3$$

$$a(A_2) = \frac{1}{6} [(1)(12)(1) + 2(0)(1) + 3(2)(-1)] = 1$$

$$a(E) = \frac{1}{6} [(1)(12)(2) + 2(0)(-1) + 3(2)(0)] = 4$$

$$\text{Hence } \Gamma_{3N} = 3A_1 + A_2 + 4E \quad (5.16.2)$$

**Problem 5.16.1**

Work out the reducible representation of methane based on the three translational vectors on each atom and resolved into irreducible representations.

**Solution** For  $\text{CH}_4$  (point group  $T_d$ ), we have

		Reducible representation					
$T_d$		$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
No. of unshifted atoms	5	5	2	1	1	1	3
		(all the five atoms)	(carbon atom and one of H atoms)	(carbon atom)	(carbon atom)	(carbon atom and two H atoms)	
$\Gamma_{3N}$	15	15	0	-1	-1	-1	3

**Irreducible representations from the character table**

	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$A_1$	1	1	1	1	1
$A_2$	1	1	1	-1	-1
$E$	2	-1	2	0	0
$T_1$	3	0	-1	1	-1
$T_2$	3	0	-1	-1	1

Thus, we have

$$a(A_1) = \frac{1}{24} [1(15)(1) + 8(0)(1) + 3(-1)(1) + 6(-1)(1) + 6(3)(1)] = 1$$

$$a(A_2) = \frac{1}{24} [1(15)(1) + 8(0)(1) + 3(-1)(1) + 6(-1)(-1) + 6(3)(-1)] = 0$$

$$a(E) = \frac{1}{24} [1(15)(2) + 8(0)(-1) + 3(-1)(2) + 6(-1)(0) + 6(3)(0)] = 1$$

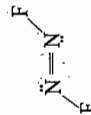
$$a(T_1) = \frac{1}{24} [1(15)(3) + 8(0)(0) + 3(-1)(-1) + 6(-1)(1) + 6(3)(-1)] = 1$$

$$a(T_2) = \frac{1}{24} [1(15)(3) + 8(0)(0) + 3(-1)(-1) + 6(-1)(-1) + 6(3)(1)] = 3$$

$$\text{Hence, } \Gamma_{3N} = A_1 + E + T_1 + 3T_2 \quad (5.16.3)$$

Work out the reducible representation of  $\text{trans-N}_2\text{F}_2$  on the basis of three translational vectors on each atom and resolve them in irreducible representations.

The structure of  $\text{N}_2\text{F}_2$  is

**Problem 5.16.2****Solution**

It belongs to the point group  $C_{2h}$ . For this molecule, we have

**Reducible representation**

$C_{2h}$	$E$	$C_2$	$i$	$\sigma_h$
Unshifted atoms	4	0	0	4
$\Gamma_{3N}$	12	0	0	4

**Irreducible representations from the character table**

$C_{2h}$	$E$	$C_2$	$i$	$\sigma_h$
$A_g$	1	1	1	1
$B_g$	1	-1	-1	-1
$A_u$	1	1	-1	-1
$B_u$	1	-1	1	1

$$a(A_g) = \frac{1}{4} [1(12)(1) + 1(0)(1) + 1(0)(1) + 1(4)(1)] = 4$$

$$a(B_g) = \frac{1}{4} [1(12)(1) + 1(0)(-1) + 1(0)(1) + 1(4)(-1)] = 2$$

$$a(A_u) = \frac{1}{4} [1(12)(1) + 1(0)(1) + 1(0)(-1) + 1(4)(-1)] = 2$$

$$a(B_u) = \frac{1}{4} [1(12)(1) + 1(0)(-1) + 1(0)(-1) + 1(4)(1)] = 4$$

$$\text{Hence } \Gamma_{3N} = 4A_g + 2B_g + 2A_u + 4B_u \quad (5.16.4)$$

**5.17 THE PROJECTION OPERATOR**

The application of group theory to simplify molecular problems involves the construction of molecular wave functions which form the bases of irreducible representations of the symmetry group of the molecule. Such a function is built by the appropriate combination of atomic wave functions and is known as symmetry-adapted linear combination (abbreviation: SALC).

The SALC's of a molecule is built by using the projection operator, defined as

$$\hat{P}_i = \frac{1}{h} \sum_R \chi_i(R) \hat{R} \quad (5.17.1)$$

where  $I_i$  is the dimension of matrices of  $i$ th irreducible representation,

$h$  is the order of the group,

$\chi_i(R)$  is the character of the matrix representing to the  $R$ th operation in the  $i$ th irreducible representation,

and  $\hat{R}$  is the operator for the symmetry operation  $R$ .

Suppose we have an orthonormal set of functions  $\phi_1^{(i)}, \phi_2^{(i)}, \dots$ , which form a basis for the  $i$ th irreducible representation (of dimension  $I_i$ ) of a group of order  $h$ . By definition, we write

$$\hat{R}\phi_s^{(i)} = \sum_r \Gamma_r^{(i)}(R) \phi_r^{(i)} \quad (5.17.2)$$

which implies that the result of symmetry operation  $\hat{R}$  on one of the functions  $\phi_s^{(i)}$  is obtained by carrying out the summation of the product of the elements of  $s$ th row of the matrix representing of the operation  $R$  in the  $i$ th irreducible representation with the corresponding basis functions†

Multiplying both sides of Eq. (5.17.2) by  $[\Gamma_i(R)_{s'r'}]^\dagger$  and summing over all operations in the group, we get

$$\sum_R [\Gamma_i(R)_{s'r'}]^\dagger \hat{R} \phi_s^{(i)} = \sum_R \sum_i [\Gamma_i(R)_{s'r'}]^\dagger \Gamma_i(R)_{st} \phi_t^{(i)}$$

Since the functions  $\phi_t^{(i)}$ 's are independent of the operation, we can rewrite the right side of the above expression as

$$\sum_R [\Gamma_i(R)_{s'r'}]^\dagger \hat{R} \phi_s^{(i)} = \sum_t \phi_t^{(i)} \left( \sum_R [\Gamma_i(R)_{s'r'}]^\dagger \Gamma_i(R)_{st} \right)$$

which on using 'The Great Orthogonality theorem' becomes

$$\sum_R [\Gamma_i(R)_{s'r'}]^\dagger \hat{R} \phi_s^{(i)} = \sum_t \phi_t^{(i)} \left[ \frac{h}{I_i} \delta_{ss'} \delta_{rr'} \right]$$

On carrying out the summation over  $t$ , only the term for which  $t = s'$  survives. Hence, we get

$$\frac{I_i}{h} \sum_R [\Gamma_i(R)_{s'r'}]^\dagger \hat{R} \phi_s^{(i)} = \phi_{s'}^{(i)} \delta_{ss'} \quad (5.17.3)$$

Defining the projection operator as

$$\hat{P}_{s'r'}^{(i)} = \frac{I_i}{h} \sum_R [\Gamma_i(R)_{s'r'}]^\dagger \hat{R} \quad (5.17.4)$$

we can write Eq. (5.17.3) as

$$\hat{P}_{s'r'}^{(i)} \phi_s^{(i)} = \phi_{s'}^{(i)} \delta_{ss'} \quad (5.17.5)$$

For  $s = s'$ , the above expression becomes

$$\hat{P}_{s'r'}^{(i)} \phi_s^{(i)} = \phi_{s'}^{(i)} \quad (5.17.6)$$

† For example, the  $C_3$  operation of the point group  $C_{3v}$  over the coordinates  $x (= \phi_1)$ ,  $y (= \phi_2)$  and  $z (= \phi_3)$  is represented as

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

In Eq. (5.17.2), if  $s = 1$ , then  $\hat{C}_3 \phi_1^{(i)} = \Gamma_i(C_3)_{11} \phi_1^{(i)} + \Gamma_i(C_3)_{12} \phi_2^{(i)} + \Gamma_i(C_3)_{13} \phi_3^{(i)}$  which in the present case becomes

$$\hat{C}_3 x = -\frac{1}{2}x - \frac{\sqrt{3}}{2}y + 0(z) \quad \text{i.e.} \quad x = \frac{1}{2}(-x - \sqrt{3}y)$$

### Illustration of Eq. (5.17.6)

Equation (5.17.6) implies that the application of the operator  $\hat{P}_{s'r'}^{(i)}$  over the function  $\phi_s^{(i)}$  projects out the function  $\phi_{s'}^{(i)}$ .

Equation (5.17.6) may be illustrated by taking an example of the group  $C_{3v}$ . If  $x$  and  $y$  coordinates form the basis of E representation, then the matrices representing different symmetry operations (see Table 5.7.3) are as follows.

$E$	$\begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}$	$C_3$	$\begin{vmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{vmatrix}$	$C_3^2$	$\begin{vmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{vmatrix}$
$\sigma_v'$	$\begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}$	$\sigma_v''$	$\begin{vmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{vmatrix}$	$\sigma_v'''$	$\begin{vmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{vmatrix}$

The effects of symmetry operations on  $x$ ,  $y$  and  $z$  are as follows.

$E$	$x$	$y$	$z$
$C_3$	$-(1/2)x - (\sqrt{3}/2)y$	$(\sqrt{3}/2)x - (1/2)y$	$z$
$C_3^2$	$-(1/2)x + (\sqrt{3}/2)y$	$-(\sqrt{3}/2)x - (1/2)y$	$z$
$\sigma_v'$	$x$	$-y$	$z$
$\sigma_v''$	$-(1/2)x - (\sqrt{3}/2)y$	$-(\sqrt{3}/2)x + (1/2)y$	$z$
$\sigma_v'''$	$-(1/2)x + (\sqrt{3}/2)y$	$(\sqrt{3}/2)x + (1/2)y$	$z$

In the present case,  $\phi_1 = x$  and  $\phi_2 = y$ .

In Eq. (5.17.6) if  $s' = 1$  and  $r' = 1$ , we will get

$$\hat{P}_{11}^{(E)} \phi_1 = \phi_1 \quad \text{i.e.} \quad \hat{P}_{11} x = x$$

This may be verified from the following explicit expressions.

$$\begin{aligned} \hat{P}_{11}^{(E)} x &= \left[ \frac{I_i}{h} \sum_R \Gamma(R)_{11} \hat{R} \right] x \\ &= \frac{I_i}{h} [\Gamma(E)_{11} \hat{E} x + \Gamma(C_3)_{11} \hat{C}_3 x + \Gamma(C_3^2)_{11} \hat{C}_3^2 x \\ &\quad + \Gamma(\sigma_v')_{11} \hat{\sigma}_v' x + \Gamma(\sigma_v'')_{11} \hat{\sigma}_v'' x + \Gamma(\sigma_v''')_{11} \hat{\sigma}_v''' x] x \\ &= \frac{2}{6} [(1)x + \left(-\frac{1}{2}\right)\left(-\frac{1}{2}x - \frac{\sqrt{3}}{2}y\right) + \left(-\frac{1}{2}\right)\left(-\frac{1}{2}x + \frac{\sqrt{3}}{2}y\right) \\ &\quad + (1)x + \left(-\frac{1}{2}\right)\left(-\frac{1}{2}x - \frac{\sqrt{3}}{2}y\right) + \left(-\frac{1}{2}\right)\left(-\frac{1}{2}x + \frac{\sqrt{3}}{2}y\right)] \\ &= \frac{2}{6} \left[ x + \frac{1}{4}x + \frac{\sqrt{3}}{4}y + \frac{1}{4}x - \frac{\sqrt{3}}{4}y + x + \frac{1}{4}x + \frac{\sqrt{3}}{4}y + \frac{1}{4}x - \frac{\sqrt{3}}{4}y \right] \\ &= \frac{2}{6} (3x) = x \end{aligned}$$

Similarly, it can be shown that

$$\begin{array}{ll} \hat{P}_{12} \phi_1 = \phi_2 & \text{i.e.} \quad \hat{P}_{12} x = y \\ \hat{P}_{21} \phi_2 = \phi_1 & \text{i.e.} \quad \hat{P}_{21} y = x \\ \hat{P}_{22} \phi_2 = \phi_2 & \text{i.e.} \quad \hat{P}_{22} y = y \end{array}$$

The expressions  $\hat{P}_{12} \phi_2$ ,  $\hat{P}_{21} \phi_1$ ,  $\hat{P}_{11} \phi_2$  and  $\hat{P}_{22} \phi_1$  will each be equal to zero as the condition of  $s = s'$  is not satisfied. This may be verified by the explicit expressions as shown for the one typical case of  $\hat{P}_{11} \phi_2$ .

$$\begin{aligned} \hat{P}_{11} \phi_2 &= \hat{P}_{11} y = \frac{I_1}{h} \sum_R \Gamma(R)_{11} \hat{R} y \\ &= \frac{I_1}{h} [\Gamma(E)_{11} \hat{E} y + \Gamma(C_3)_{11} \hat{C}_3 y + \Gamma(C_3^2)_{11} \hat{C}_3^2 y + \Gamma(\sigma_v')_{11} \hat{\sigma}_v' y \\ &\quad + \Gamma(\sigma_v'')_{11} \hat{\sigma}_v'' y + \Gamma(\sigma_v''')_{11} \hat{\sigma}_v''' y] \\ &= \frac{2}{6} \left[ (1)y + \left(-\frac{1}{2}\right) \left(\frac{\sqrt{3}}{2} x - \frac{1}{2} y\right) + \left(-\frac{1}{2}\right) \left(-\frac{\sqrt{3}}{2} x - \frac{1}{2} y\right) \right. \\ &\quad \left. + (1)(-y) + \left(-\frac{1}{2}\right) \left(-\frac{\sqrt{3}}{2} x + \frac{1}{2} y\right) + \left(-\frac{1}{2}\right) \left(\frac{\sqrt{3}}{2} x + \frac{1}{2} y\right) \right] \\ &= \frac{2}{6} \left[ y - \frac{\sqrt{3}}{4} x + \frac{1}{4} y + \frac{\sqrt{3}}{4} x + \frac{1}{4} y - y + \frac{\sqrt{3}}{4} x - \frac{1}{4} y - \frac{\sqrt{3}}{4} x + \frac{1}{4} y \right] \\ &= 0 \end{aligned}$$

**Note:** Had we taken the function  $x + y$ , even then we will have

$$\begin{aligned} \hat{P}_{11}(x + y) &= \hat{P}_{11} x + \hat{P}_{11} y = x + 0 = x \\ \hat{P}_{22}(x + y) &= \hat{P}_{22} x + \hat{P}_{22} y = 0 + y = y \end{aligned}$$

This implies that  $\phi_s^{(i)}$  in Eq. (5.17.6) may be any arbitrary function. The effect of projection operator on the function is to project out the term  $\phi_s^{(i)}$  if present in the function, otherwise the result will be zero.

In Eq. (5.17.4), the projection operator is expressed in terms of individual elements of the matrices of symmetry operations. It is advantageous to express the projection operator in terms of characters, since these are normally available in a character table. For one-dimensional representations, Eq. (5.17.4), in fact, involves characters as the matrices are of  $1 \times 1$  dimensions.

For two- and three-dimensional representations, we can write

$$\begin{aligned} \hat{P}_i &= \sum_{s', s''} \hat{P}_{s', s''}^{(i)} = \frac{I_i}{h} \sum_{s'} \sum_R [\Gamma_i(R)_{s's'}]^* \hat{R} \\ &= \frac{I_i}{h} \sum_R \left\{ \sum_{s'} [\Gamma_i(R)_{s's'}]^* \hat{R} \right\} \end{aligned}$$

which on using Eq. (5.17.1) becomes

$$\hat{P}_i = \frac{I_i}{h} \sum_R \chi_i(R) \hat{R} \quad (5.17.7)$$

## Illustration

Equation (5.17.7) may be illustrated by applying the projection operators of irreducible representations of the point group  $C_{3v}$  to the function  $x + y + z$ .

- For the  $A_1$  representation, we have  $\chi(E) = 1$ ,  $\chi(C_3) = 1$  and  $\chi(\sigma_v) = 1$ . Thus

$$\begin{aligned} \hat{P}_{A_1}(x + y + z) &= \frac{I_{A_1}}{h} [\chi(E) \hat{E}(x + y + z) + \chi(C_3) \hat{C}_3(x + y + z) \\ &\quad + \chi(C_3^2) \hat{C}_3^2(x + y + z) + \chi(\sigma_v') \hat{\sigma}_v'(x + y + z) \\ &\quad + \chi(\sigma_v'') \hat{\sigma}_v''(x + y + z) + \chi(\sigma_v''') \hat{\sigma}_v'''(x + y + z)] \\ &= \frac{1}{6} \left[ (1)(x + y + z) + (1) \left\{ \left(-\frac{1}{2} x - \frac{\sqrt{3}}{2} y\right) + \left(\frac{\sqrt{3}}{2} x - \frac{1}{2} y\right) + z \right\} \right. \\ &\quad \left. + (1) \left\{ \left(-\frac{1}{2} x + \frac{\sqrt{3}}{2} y\right) + \left(-\frac{\sqrt{3}}{2} x - \frac{1}{2} y\right) + z \right\} + (1)(x - y + z) \right. \\ &\quad \left. + (1) \left\{ \left(-\frac{1}{2} x - \frac{\sqrt{3}}{2} y\right) + \left(-\frac{\sqrt{3}}{2} x + \frac{1}{2} y\right) + z \right\} \right. \\ &\quad \left. + (1) \left\{ \left(-\frac{1}{2} x + \frac{\sqrt{3}}{2} y\right) + \left(\frac{\sqrt{3}}{2} x + \frac{1}{2} y\right) + z \right\} \right] \\ &= \frac{1}{6} (6z) = z \end{aligned}$$

Hence, the projection operator for  $A_1$  representation projects the coordinate  $z$  (and not  $x$  and  $y$ ). Hence, the coordinate  $z$  forms the basis of  $A_1$  representation.

- For the  $E$  representation, we have  $\chi(E) = 2$ ,  $\chi(C_3) = -1$  and  $\chi(\sigma_v) = 0$ . Thus

$$\begin{aligned} \hat{P}_E(x + y + z) &= \frac{I_E}{h} [\chi(E) \hat{E}(x + y + z) + \chi(C_3) \hat{C}_3(x + y + z) \\ &\quad + \chi(C_3^2) \hat{C}_3^2(x + y + z) + \chi(\sigma_v') \hat{\sigma}_v'(x + y + z) \\ &\quad + \chi(\sigma_v'') \hat{\sigma}_v''(x + y + z) + \chi(\sigma_v''') \hat{\sigma}_v'''(x + y + z)] \\ &= \frac{2}{6} \left[ (2)(x + y + z) + (-1) \left\{ \left(-\frac{1}{2} x - \frac{\sqrt{3}}{2} y\right) + \left(\frac{\sqrt{3}}{2} x - \frac{1}{2} y\right) + z \right\} \right. \\ &\quad \left. + (-1) \left\{ \left(-\frac{1}{2} x + \frac{\sqrt{3}}{2} y\right) + \left(-\frac{\sqrt{3}}{2} x - \frac{1}{2} y\right) + z \right\} \right] \\ &= \frac{2}{6} (3x + 3y) = x + y \end{aligned}$$

Thus, the projection operator for the  $E$  representation projects the coordinates  $x$  and  $y$  (and not  $z$ ). Thus,  $x$  and  $y$  taken together form the bases of  $E$  representation.

From the above two illustrations, it is obvious that the projection operator when applied to a function annihilates the element that does not contribute to a given irreducible representation.

## 5.18 WORKED OUT EXAMPLES OF SALC'S AND MO'S

A BENT AX<sub>2</sub> MOLECULE (EXAMPLE: H<sub>2</sub>O)

A bent AX<sub>2</sub> molecule belongs to the point group C<sub>2v</sub>. The common example is H<sub>2</sub>O molecule (Fig. 5.18.1).

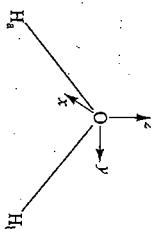


Fig. 5.18.1 H<sub>2</sub>O molecule with cartesian axes on oxygen atom

## Nature of Irreducible Representations

- From the character table of the group C<sub>2v</sub>, we find the following facts.
  - (i) 2s(O) and 2p<sub>z</sub>(O) orbitals belong to a<sub>1</sub> irreducible representation†
  - (ii) 2p<sub>x</sub>(O) orbital belongs to b<sub>1</sub> irreducible representation
  - (iii) 2p<sub>y</sub>(O) orbital belongs to b<sub>2</sub> irreducible representation
- The symmetries of possible combinations of 1s orbitals of hydrogen atoms are determined as follows.

The reducible representation obtained on the basis of 1s(H<sub>a</sub>) and 1s(H<sub>b</sub>) is

C <sub>2v</sub>	E	C <sub>2</sub>	σ(xz)	σ(yz)
Γ	2	0	0	2
	(both the orbitals remain unshifted)	(orbitals exchange positions)	(orbitals exchange positions)	(both the orbitals remain unshifted)

The use of reduction formula  $a_i = \frac{1}{h} \sum_R \chi_i(R) \chi_i(R)$  gives

$$a(a_1) = \frac{1}{4} [(2)(1) + (0)(1) + (0)(1) + (2)(1)] = 1$$

$$a(a_2) = \frac{1}{4} [(2)(1) + (0)(1) + (0)(-1) + (2)(-1)] = 0$$

$$a(b_1) = \frac{1}{4} [(2)(1) + (0)(-1) + (0)(1) + 2(-1)] = 0$$

$$a(b_2) = \frac{1}{4} [(2)(-1) + (0)(-1) + (0)(-1) + 2(1)] = 1$$

Hence  $\Gamma = a_1 + b_2$  (5.18.1)

The symmetry-adapted linear combinations of 1s(H<sub>a</sub>) and 1s(H<sub>b</sub>) orbitals can be constructed by using the projection operator

$$\hat{P}_i = \frac{1}{h} \sum_R \chi_i(R) \hat{R} \quad (5.18.2)$$

† Lower case Mulliken symbols are used to represent irreducible representations for one-electron atomic orbitals.

on the generating function  $\psi_{1s(H_a)}$ , we have

$$\begin{aligned} \hat{P}_{a_1} \psi_{1s(H_a)} &= \frac{1}{4} [\chi_{a_1}(E) \{\hat{E} \psi_{1s(H_a)}\} + \chi_{a_1}(C_2) \{\hat{C}_2 \psi_{1s(H_a)}\} \\ &\quad + \chi_{a_1}(\sigma_{xz}) \{\hat{\sigma}_{xz} \psi_{1s(H_a)}\} + \chi_{a_1}(\sigma_{yz}) \{\hat{\sigma}_{yz} \psi_{1s(H_a)}\}] \end{aligned}$$

$$= \frac{1}{4} [(1) \psi_{1s(H_a)} + (1) \psi_{1s(H_b)} + (1) \psi_{1s(H_b)} + (1) \psi_{1s(H_a)}]$$

$$\text{i.e. } \phi'_1 = \frac{1}{2} [\psi_{1s(H_a)} + \psi_{1s(H_b)}]$$

The factor 1/2 in the above expression may be ignored as it provides the relative values resulting from the operators. The absolute values may be determined by the normalization of the wavefunction. The expression of normalized function is

$$\phi_1 = \frac{1}{\sqrt{2}} [\psi_{1s(H_a)} + \psi_{1s(H_b)}] \quad (5.18.3)$$

Similarly, we have

$$\hat{P}_{b_2} \psi_{1s(H_a)} = \frac{1}{4} [(1) \psi_{1s(H_a)} + (-1) \psi_{1s(H_b)} + (-1) \psi_{1s(H_b)} + (1) \psi_{1s(H_a)}]$$

$$\text{i.e. } \phi_2 = \frac{1}{2} [\psi_{1s(H_a)} - \psi_{1s(H_b)}]$$

The expression of normalized function is

$$\phi_2 = \frac{1}{\sqrt{2}} [\psi_{1s(H_a)} - \psi_{1s(H_b)}] \quad (5.18.4)$$

The molecular orbitals of H<sub>2</sub>O can be constructed by mixing atomic orbitals of oxygen with the correct symmetry-adapted linear combination of 1s orbitals of hydrogen atoms.

Mixing of orbitals of a<sub>1</sub> irreducible representation

$$\begin{aligned} \psi_{1,2,3} &= C_1 \psi_{2s(O)} + C_2 \psi_{2p_z(O)} + C_3 \phi_1 \\ &= C_1 \psi_{2s(O)} + C_2 \psi_{2p_z(O)} + C_3 [\psi_{1s(H_a)} + \psi_{1s(H_b)}] \end{aligned} \quad (5.18.5)$$

This combination yields three molecular orbitals, one strongly bonding, one slightly bonding and one strongly antibonding.

Mixing of orbitals of b<sub>2</sub> irreducible representation

$$\begin{aligned} \psi_4 &= C_4 \psi_{2p_y(O)} + C_5 \phi_2 = C_4 \psi_{2p_y(O)} + C_5 [\psi_{1s(H_a)} - \psi_{1s(H_b)}] \quad (5.18.6) \\ \psi_5 &= C_6 \psi_{2p_x(O)} - C_7 [\psi_{1s(H_a)} - \psi_{1s(H_b)}] \end{aligned} \quad (5.18.7)$$

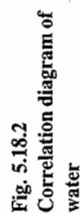
The plus combination with C<sub>4</sub> > C<sub>5</sub> yields bonding molecular orbital and negative combination with C<sub>7</sub> > C<sub>6</sub> yields antibonding molecular orbital.

The atomic orbital  $\psi_{2p_x(O)}$  acts as nonbonding orbital.

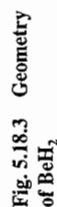
## Molecular Orbitals of Water



The correlation diagram of water is shown in Fig. 5.18.2.



A linear  $AX_2$  molecule belongs to the  $D_{\infty h}$  point group. The common example is  $BeH_2$  molecule (Fig. 5.18.3).



(i)  $2s(\text{Be})$  belongs to  $\Sigma^+$  irreducible representation.

(ii)  $2p_{\pi}(\text{Be})$  belongs to  $\Sigma^+$  irreducible representation.

(iii)  $2p_r(\text{Be})$  and  $2p_v(\text{Be})$  belong to  $\Pi_n$  irreducible representation.

- The reducible representation obtained on the basis of  $1s(H_a)$  and  $1s(H_b)$  is

### Nature of Irreducible Representations

It is not possible to resolve the above reducible representation into irreducible representations of the group  $D_{\infty h}$  because  $h = \infty$ . It is, therefore, necessary to carry out the resolution by inspection of the character table. We find that

$$\Gamma = \sigma_1^+ + \sigma_2^+ + \sigma_3^+ \quad (5.18.8)$$

### Molecular Orbitals of BeH<sub>2</sub>

$$\sigma_g^+ \text{ symmetry: } \phi_1 = \frac{1}{\sqrt{2}} [\psi_{1s(H_a)} + \psi_{1s(H_b)}] \quad (5.18.9)$$

$$\sigma_u^+ \text{ symmetry: } \varphi_2 = \frac{1}{\sqrt{2}} \left[ \psi_{1s(H_a)} - \psi_{1s(H_b)} \right] \quad (5.18.10)$$

where the factor  $1/\sqrt{2}$  in each of the above two expressions is normalization constant.

The molecular orbitals of  $\text{BeH}_2$  can be constructed by mixing atomic orbitals of beryllium with the correct symmetry-adapted linear combination of 1s orbitals of hydrogen atoms.

**Mixing of orbitals of  $\sigma^+$  irreducible representation** We have

$$\psi_1 = C_1 \psi_{2s(O)} + C_2 \varphi_1 = C_1 \psi_{2s(O)} + C_2 [\psi_{1s(H_a)} + \psi_{1s(H_b)}] \quad (5.18.11)$$

$$\psi_2 = C_3 \psi_{2s(O)} - C_4 \phi_1 = C_3 \psi_{2s(O)} - C_4 [\psi_{1s(H_s)} + \psi_{1s(H_b)}] \quad (5.18.12)$$

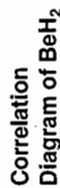
**Mixing of orbitals of  $\sigma_u^+$  irreducible representation** We have

$$\psi_3 = C_5 \psi_{2p, (\text{Be})} + C_6 \phi_2 = C_5 \psi_{2p, (\text{Be})} + C_6 [\psi_{1s(\text{H}_a)} - \psi_{1s(\text{H}_b)}] \quad (5.18.13)$$

$$\psi_4 = C_7 \psi_{2p,(\text{Be})} - C_8 \varphi_2 = C_7 \psi_{2p,(\text{Be})} - C_8 [\psi_{1s(\text{H}_2)} - \psi_{1s(\text{H}_b)}] \quad (5.18.14)$$

The atomic orbitals  $\psi_{2a_{1g}(B_{2g})}$  and  $\psi_{2a_{1g}(B_{2g})}$  act as nonbonding orbitals.

The correlation diagram of  $\text{BeH}_2$  is shown in Fig. 5.18.4.



**Fig. 5.18.4**  
**Correlation diagram of**  
**BeH<sub>2</sub>**

<sup>†</sup> See example of H<sub>2</sub>O.

**A PLANAR AX<sub>3</sub> MOLECULE (EXAMPLE: BH<sub>3</sub>)**

A planar AX<sub>3</sub> molecule belongs to the D<sub>3h</sub> point group. The common example is BH<sub>3</sub> molecule (Fig. 5.18.5).

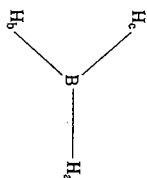


Fig. 5.18.5 Geometry of BH<sub>3</sub>

**Nature of Irreducible Representations**

- From the character table of the D<sub>3h</sub> group, we find the following facts.
  - (i) s(B) orbital belongs to a<sub>1</sub>' irreducible representation.
  - (ii) p<sub>z</sub>(B) orbital belongs to a<sub>2</sub>' irreducible representation.
  - (iii) p<sub>x</sub>(B) and p<sub>y</sub>(B) orbitals belong to e' irreducible representation.
- The symmetries of possible combinations of 1s orbitals of hydrogen atoms are determined as follows.

The reducible representation obtained on the basis of 1s(H<sub>a</sub>), 1s(H<sub>b</sub>) and 1s(H<sub>c</sub>) is

D <sub>3h</sub>	E	2C <sub>3</sub>	3C <sub>2</sub>	σ <sub>h</sub>	2S <sub>3</sub>	3σ <sub>v</sub>
Γ	3	0	1	3	0	1 (= number of unshifted orbitals)
	The three orbitals remain unshifted	All the three orbitals are shifted	One of the orbitals remains unshifted	The three orbitals remain unshifted	All the three orbitals are shifted	One of the orbitals remains unshifted

The use of reduction formula  $a_i = \frac{1}{h} \sum_C n_C \chi(C) \chi_i(C)$  gives

$$a(a_1') = \frac{1}{12} [(3)(1) + 2(0)(1) + 3(1)(1) + (3)(1) + 2(0)(1) + 3(1)(1)] = 1$$

$$a(e') = \frac{1}{12} [(3)(2) + 2(0)(-1) + 3(1)(0) + (3)(2) + 2(0)(-1) + 3(1)(0)] = 1$$

This also follows by inspection of character table since the addition of corresponding characters of a<sub>1</sub>' and e' gives the characters of reducible representation. Hence

$$\Gamma = a_1' + e' \quad (5.18.15)$$

The symmetry-adapted linear combinations of 1s(H<sub>a</sub>), 1s(H<sub>b</sub>) and 1s(H<sub>c</sub>) orbitals can be constructed by using the expression

$$\hat{P}_i \phi = \frac{1}{h} \sum_R \chi_i(R) \{\hat{R} \phi\}$$

or simply by the expression

$$\hat{P}_i \phi = \sum_R \chi_i(R) \{\hat{R} \phi\}$$

as the coefficients of atomic orbitals in the resultant SALC are determined by the normalization procedure. Taking  $\phi$  as  $\psi_{1s(H_a)}$ , we get

$$\begin{aligned} \hat{P}_{a_1'} \psi_{1s(H_a)} &= \chi_{a_1'}(E) \{\hat{E} \psi_{1s(H_a)}\} + \chi_{a_1'}(C_3) [\hat{C}_3 \psi_{1s(H_a)} + \hat{C}_3^2 \psi_{1s(H_b)}] \\ &\quad + \chi_{a_1'}(C_2) [\hat{C}_2 \psi_{1s(H_a)} + \hat{C}_2^2 \psi_{1s(H_b)} + \hat{C}_2^2 \psi_{1s(H_c)}] \\ &\quad + \chi_{a_1'}(\sigma_h) \{\hat{\sigma}_h \psi_{1s(H_a)}\} + \chi_{a_1'}(S_3) [\hat{S}_3 \psi_{1s(H_a)} + \hat{S}_3^2 \psi_{1s(H_b)}] \\ &\quad + \chi_{a_1'}(\sigma_v) [\hat{\sigma}_v \psi_{1s(H_a)} + \hat{\sigma}_v' \psi_{1s(H_b)} + \hat{\sigma}_v'' \psi_{1s(H_c)}] \\ &= (1) \psi_{1s(H_a)} + (1) \{\psi_{1s(H_b)} + \psi_{1s(H_c)}\} \\ &\quad + (1) \{\psi_{1s(H_a)} + \psi_{1s(H_b)} + \psi_{1s(H_c)}\} + (1) \psi_{1s(H_a)} \\ &\quad + (1) \{\psi_{1s(H_b)} + \psi_{1s(H_c)}\} + (1) \{\psi_{1s(H_a)} + \psi_{1s(H_b)} + \psi_{1s(H_c)}\} \\ &= 4[\psi_{1s(H_a)} + \psi_{1s(H_b)} + \psi_{1s(H_c)}] \end{aligned}$$

The expression of normalized SALC is

$$\phi_1 = \frac{1}{\sqrt{3}} [\psi_{1s(H_a)} + \psi_{1s(H_b)} + \psi_{1s(H_c)}] \quad (5.18.16)$$

The operation of  $\hat{P}_{e'}$  on  $\psi_{1s(H_a)}$  gives

$$\begin{aligned} \hat{P}_{e'} \psi_{1s(H_a)} &= (2) \psi_{1s(H_a)} + (-1) \{\psi_{1s(H_b)} + \psi_{1s(H_c)}\} \\ &\quad + (0) \{\psi_{1s(H_a)} + \psi_{1s(H_b)} + \psi_{1s(H_c)}\} + (2) \psi_{1s(H_a)} \\ &\quad + (-1) \{\psi_{1s(H_b)} + \psi_{1s(H_c)}\} + (0) \{\psi_{1s(H_a)} + \psi_{1s(H_b)} + \psi_{1s(H_c)}\} \\ &= 4 \psi_{1s(H_a)} - 2 \psi_{1s(H_b)} - 2 \psi_{1s(H_c)} \end{aligned}$$

The expression of normalized SALC is

$$\phi_2 = \frac{1}{\sqrt{6}} [2\psi_{1s(H_a)} - \psi_{1s(H_b)} - \psi_{1s(H_c)}] \quad (5.18.17)$$

Note that the SALC  $\phi_2$  is orthogonal to the SALC  $\phi_1$ .

Since e' representation contains doubly generate orbitals, we may generate the second SALC by using either of the orbitals  $\psi_{1s(H_b)}$  and  $\psi_{1s(H_c)}$ . The operation  $\hat{P}_{e'}$  on these orbitals would give

$$\begin{aligned} \phi_3' &= \frac{1}{\sqrt{6}} [2\psi_{1s(H_b)} - \psi_{1s(H_a)} - \psi_{1s(H_c)}] \\ \phi_3'' &= \frac{1}{\sqrt{6}} [2\psi_{1s(H_c)} - \psi_{1s(H_a)} - \psi_{1s(H_b)}] \end{aligned}$$

But neither  $\phi_3'$  nor  $\phi_3''$  is orthogonal to  $\phi_2$ . However, if we take linear combination  $\phi_3' - \phi_3''$ , the resultant expression is orthogonal to  $\phi_2$ . The expression of normalized second orbital in e' representation is

$$\phi_3 = \frac{1}{\sqrt{2}} [\psi_{1s(H_b)} - \psi_{1s(H_c)}] \quad (5.18.18)$$

**Note:** The combination  $\phi'_3 + \phi''_3$  results into the function  $\phi_2$ , which may thus be excluded.

### Alternative Procedure

Instead of using full symmetry of the point group  $C_{3v}$ , the SALC's may be derived by using only the pure rotational symmetry, i.e. rotation about the principal axis. In the present case, we have

$$\hat{P}_a \psi_{1s(H_A)} = \chi_a(E) \{ \hat{E} \psi_{1s(H_A)} \} + \chi_a(C_3) \{ \hat{C}_3 \psi_{1s(H_A)} \} + \chi_a(C_3^2) \{ \hat{C}_3^2 \psi_{1s(H_A)} \}$$

$$\text{i.e. } \phi'_1 = (1) \psi_{1s(H_A)} + (1) \psi_{1s(H_B)} + (1) \psi_{1s(H_C)}$$

$$\phi''_2 = \hat{P}_e \psi_{1s(H_A)} = (1) \psi_{1s(H_A)} + (\varepsilon) \psi_{1s(H_B)} + (\varepsilon^*) \psi_{1s(H_C)}$$

$$\phi''_3 = \hat{P}_e \psi_{1s(H_A)} = (1) \psi_{1s(H_A)} + (\varepsilon^*) \psi_{1s(H_B)} + (\varepsilon) \psi_{1s(H_C)}$$

where  $\varepsilon = \cos(2\pi/3) + i \sin(2\pi/3)$  and  $\varepsilon^* = \cos(2\pi/3) - i \sin(2\pi/3)$

The imaginary quantities in  $\phi''_2$  and  $\phi''_3$  can be removed as follows.

$$\begin{aligned} \phi'_2 &= \phi''_2 + \phi''_3 = 2\psi_{1s(H_A)} + 2\cos(2\pi/3) \{ \psi_{1s(H_B)} + \psi_{1s(H_C)} \} \\ &= 2\psi_{1s(H_A)} - \psi_{1s(H_B)} - \psi_{1s(H_C)} \\ \phi'_3 &= \frac{\phi''_2 - \phi''_3}{i} = 2\sin(2\pi/3) \{ \psi_{1s(H_B)} - \psi_{1s(H_C)} \} \\ &= \sqrt{3} \{ \psi_{1s(H_B)} - \psi_{1s(H_C)} \} \end{aligned}$$

These SALC's may be normalized to obtain the new set of coefficients.

The molecular orbitals of  $BH_3$  can be constructed by mixing of atomic orbitals of B with the correct symmetry-adapted linear combination of 1s orbitals of hydrogen atoms.

### Mixing of orbitals of $a_1$ irreducible representations

$$\psi_1 = C_1 \psi_{2s(B)} + C_2 [\psi_{1s(H_A)} + \psi_{1s(H_B)} + \psi_{1s(H_C)}] \quad (5.18.19)$$

$$\psi_2^* = C_3 \psi_{2s(B)} - C_4 [\psi_{1s(H_A)} + \psi_{1s(H_B)} + \psi_{1s(H_C)}] \quad (5.18.20)$$

### Mixing of orbitals of $e'$ irreducible representations

$$\psi_3 = C_5 [\psi_{2p_x(B)} + \psi_{2p_y(B)}] + C_6 [\psi_{1s(H_A)} - \psi_{1s(H_B)} - \psi_{1s(H_C)}] \quad (5.18.21)$$

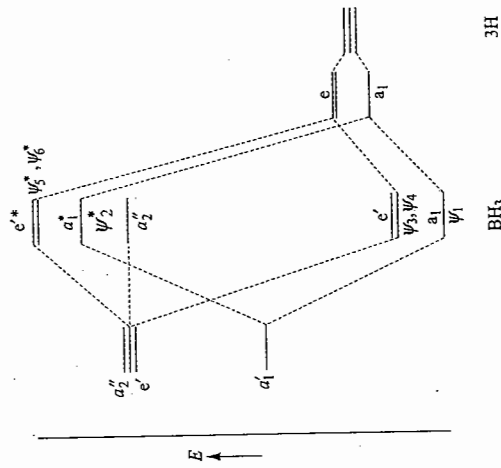
$$\psi_4 = C_5 [\psi_{2p_x(B)} - \psi_{2p_y(B)}] + C_6 [\psi_{1s(H_A)} - \psi_{1s(H_B)}] \quad (5.18.22)$$

$$\psi_5^* = C_7 [\psi_{2p_x(B)} + \psi_{2p_y(B)}] - C_8 [\psi_{1s(H_A)} - \psi_{1s(H_B)} - \psi_{1s(H_C)}] \quad (5.18.23)$$

$$\psi_6^* = C_7 [\psi_{2p_x(B)} - \psi_{2p_y(B)}] - C_8 [\psi_{1s(H_A)} - \psi_{1s(H_C)}] \quad (5.18.24)$$

The orbital  $\phi_{2p_x(B)}$  acts as nonbonding molecular orbital.

**Correlation Diagram of  $BH_3$**   
The correlation diagram of  $BH_3$  is shown in Fig. 5.18.6.



**Fig. 5.18.6**  
Correlation diagram of  $BH_3$

### A POLAR $AX_3$ MOLECULE (EXAMPLE: $NH_3$ )

The point group of  $NH_3$  is  $C_{3v}$ . From its character table, we find that  
(i)  $s(N)$  and  $p_z$  orbitals belong to  $a_1$  irreducible representation.

(ii)  $p_x$  and  $p_y$  orbitals belong to  $e$  irreducible representation.

- The reducible representation obtained on the basis of  $1s(H_A)$ ,  $1s(H_B)$  and  $1s(H_C)$  is

$C_{3v}$	$E$	$2C_3$	$3C_2$	$3\sigma_v$
$\Gamma$	3	0	1	1 (= number of unshifted orbitals)
	(All the three orbitals remain unshifted)	(All the three orbitals are shifted)	(One of the $1s(H)$ orbitals remains unshifted)	

- The use of reduction formula gives

$$a(a_1) = \frac{1}{6} [(3)(1) + 2(0)(1) + 3(1)(1)] = 1 \quad (5.18.25)$$

$$a(e) = \frac{1}{6} [(3)(2) + 2(0)(-1) + 3(1)(0)] = 1 \quad (5.18.26)$$

Thus  $\Gamma = a_1 + e$

The symmetry-adapted linear combinations of  $1s(H_A)$ ,  $1s(H_B)$  and  $1s(H_C)$  orbitals can be worked out and are found to be identical to those of  $BH_3$ . These are:

$$a_1 \text{ symmetry} \quad \phi_1 = \frac{1}{\sqrt{3}} [\psi_{1s(H_A)} + \psi_{1s(H_B)} + \psi_{1s(H_C)}] \quad (5.18.27)$$

$$e \text{ symmetry} \quad \phi_2 = \frac{1}{\sqrt{6}} [2\psi_{1s(H_A)} - \psi_{1s(H_B)} - \psi_{1s(H_C)}] \quad (5.18.28)$$

### Molecular Orbitals of NH<sub>3</sub>

The molecular orbitals of NH<sub>3</sub> can be constructed by mixing of atomic orbitals of N with the correct symmetry-adapted linear combination of 1s orbitals of hydrogen atoms.

$$\phi_3 = \frac{1}{\sqrt{2}} [\psi_{1s(H_a)} - \psi_{1s(H_c)}] \quad (5.18.29)$$

**Mixing of orbitals of a<sub>1</sub> symmetry** Mixing of 2s(N) and 2p<sub>z</sub>(N) with the group orbital  $\phi_1$  leads to the formation of three molecular orbitals.

$$\psi_1 = C_1 \psi_{2s(N)} + C_2 \psi_{2p_z(N)} + C_3 [\psi_{1s(H_a)} + \psi_{1s(H_b)} + \psi_{1s(H_c)}] \quad (5.18.30)$$

$$\psi_2 = C'_1 \psi_{2s(N)} - C'_2 \psi_{2p_z(N)} + C'_3 [\psi_{1s(H_a)} + \psi_{1s(H_b)} + \psi_{1s(H_c)}] \quad (5.18.31)$$

$$\psi_3 = C''_1 \psi_{2s(N)} - C''_2 \psi_{2p_z(N)} - C''_3 [\psi_{1s(H_a)} + \psi_{1s(H_b)} + \psi_{1s(H_c)}] \quad (5.18.32)$$

#### Mixing of orbitals of e symmetry

$$\psi_4 = C_4 \psi_{2p_x(N)} + C_5 [2\psi_{1s(H_a)} - \psi_{1s(H_b)} - \psi_{1s(H_c)}] \quad (5.18.33)$$

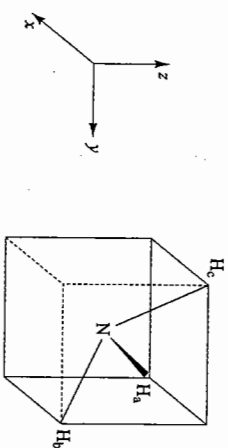
$$\psi_5 = C'_4 \psi_{2p_x(N)} - C'_5 [2\psi_{1s(H_a)} - \psi_{1s(H_b)} - \psi_{1s(H_c)}] \quad (5.18.34)$$

$$\psi_6 = C_6 \psi_{2p_y(N)} + C_7 [\psi_{1s(H_a)} - \psi_{1s(H_c)}] \quad (5.18.35)$$

$$\psi_7 = C'_6 \psi_{2p_y(N)} - C'_7 [\psi_{1s(H_a)} - \psi_{1s(H_c)}] \quad (5.18.36)$$

A molecule of ammonia may be depicted within a cube (Fig. 5.18.7). The nitrogen atom lies at the centre of the cube which is considered to be the origin of the Cartesian axes pointing towards the centres of the faces of the cube. If the edge length of the cube is unity, the three hydrogen atoms may be considered to occupy the positions (1/2, 1/2, 1/2), (-1/2, 1/2, -1/2) and (-1/2, -1/2, 1/2), respectively.

Fig. 5.18.7 Ammonia molecule within a cube



Each of the three localized molecular orbitals in ammonia may be considered to involve the sp<sup>3</sup> hybrid orbital of nitrogen and 1s orbital of hydrogen atom. These combinations may be obtained by the linear combinations of nonlocalized molecular orbitals as shown in the following.

### Correlation Diagrams of NH<sub>3</sub>

The correlation diagrams of nonlocalized and localized molecular orbitals of NH<sub>3</sub> are shown in Fig. 5.18.8.

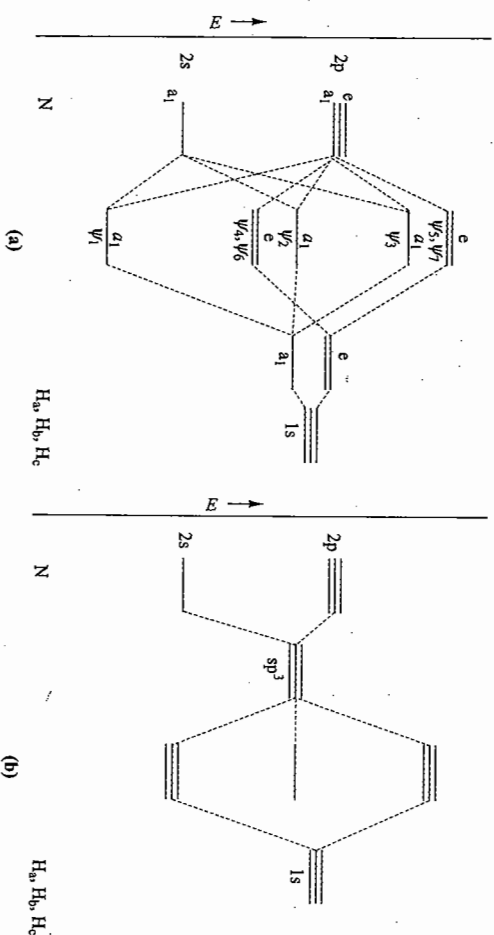


Fig. 5.18.8 Correlation diagrams depicting (a) nonlocalized and (b) localized molecular orbitals of NH<sub>3</sub>

$$\psi_{N-H_a} = \psi_1 + \psi_4 + \psi_6$$

$$= C_1 \psi_{2s(N)} + C_2 \psi_{2p_z(N)} + C_4 \psi_{2p_x(N)} + C_6 \psi_{2p_y(N)} + (C_3 + 2C_5) \psi_{1s(H_a)} + (C_3 - C_5 + C_7) \psi_{1s(H_b)} + (C_3 - C_5 - C_7) \psi_{1s(H_c)}$$

Assuming  $C_3 - C_5 + C_7$  and  $C_3 - C_5 - C_7$  to be negligible in comparison to  $C_3 + 2C_5$ , we get

$$\psi_{N-H_a} = C_1 \psi_{2s(N)} + C_2 \psi_{2p_z(N)} + C_4 \psi_{2p_x(N)} + C_6 \psi_{2p_y(N)} + (C_3 + 2C_5) \psi_{1s(H_a)} \quad (5.18.37)$$

Similarly, we get

$$\psi_{N-H_b} = \psi_2 - \psi_4 + \psi_6$$

$$= C'_1 \psi_{2s(N)} - C'_2 \psi_{2p_z(N)} - C_4 \psi_{2p_x(N)} + C_6 \psi_{2p_y(N)} + (C'_3 + C_5 + C_7) \psi_{1s(H_b)} \quad (5.18.38)$$

$$\psi_{N-H_c} = \psi_1 - \psi_4 - \psi_6$$

$$= C_1 \psi_{2s(N)} + C_2 \psi_{2p_z(N)} - C_4 \psi_{2p_x(N)} - C_6 \psi_{2p_y(N)} + (C_3 + C_5 + C_7) \psi_{1s(H_c)} \quad (5.18.39)$$

## MOLECULAR ORBITAL TREATMENT OF METHANE

### Depiction of CH<sub>4</sub> Molecule

A molecule of methane may be depicted within a cube (Fig. 5.18.9). The carbon atom lies at the centre of the cube which is considered to be the origin of the Cartesian axes pointing towards the centres of the faces of the cube. If the edge length of the cube is unity, the hydrogen atoms lie at  $(1/2, 1/2, 1/2)$ ,  $(1/2, -1/2, -1/2)$ ,  $(-1/2, -1/2, 1/2)$  and  $(-1/2, 1/2, 1/2)$ , respectively.

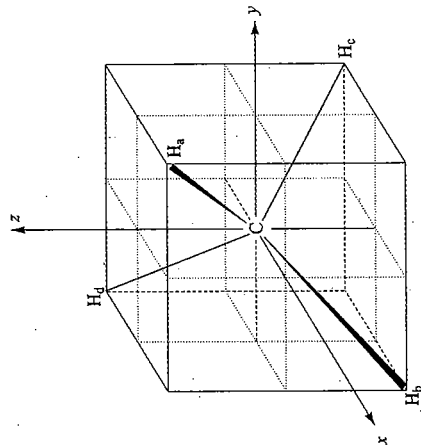


Fig. 5.18.9 Methane molecule

### Valence Orbitals of Molecule

The valence orbitals of carbon and hydrogen atoms to be considered for the treatment of molecular orbitals are  $2s(C)$ ,  $2p_x(C)$ ,  $2p_y(C)$ ,  $2p_z(C)$ ,  $1s(H_1)$ ,  $1s(H_2)$  and  $1s(H_3)$ , respectively.

The point group of methane is  $T_d$ . The atomic orbital  $2s(C)$  belongs to the representation  $a_1$ . The atomic orbitals  $2p_x(C)$ ,  $2p_y(C)$  and  $2p_z(C)$  belong to the representation,  $t_2$ ; each of these orbitals is sent into some linear combination of the three orbitals by each symmetry operation of the point group.

To describe the mixing of carbon orbitals with  $1s$  orbitals of hydrogen atom, we form the following four group orbitals.

$$\psi' = \psi_{1s(H_1)} + \psi_{1s(H_2)} + \psi_{1s(H_3)} + \psi_{1s(H_4)} \quad (5.18.40)$$

$$\psi'_x = \psi_{1s(H_1)} + \psi_{1s(H_2)} - \psi_{1s(H_3)} - \psi_{1s(H_4)} \quad (5.18.41)$$

$$\psi'_y = \psi_{1s(H_1)} - \psi_{1s(H_2)} + \psi_{1s(H_3)} - \psi_{1s(H_4)} \quad (5.18.42)$$

$$\psi'_z = \psi_{1s(H_1)} - \psi_{1s(H_2)} - \psi_{1s(H_3)} + \psi_{1s(H_4)} \quad (5.18.43)$$

The group orbital  $\psi'$  behaves as  $A_1$  representation whereas  $\psi'_x$ ,  $\psi'_y$  and  $\psi'_z$  behave at  $T_2$  representations. The subscripts  $x$ ,  $y$  and  $z$  indicate that the functions  $\psi'_x$ ,  $\psi'_y$  and  $\psi'_z$  have the same symmetry behaviour as  $x$ -,  $y$ - and  $z$ -coordinates, respectively.

and each of these functions is sent into some linear combinations of these orbitals by each symmetry operations of the group.

Combining the carbon orbitals with the group orbitals involving hydrogen atoms of the appropriate symmetry results into the following eight molecular orbitals.

### Molecular orbitals of $A_1$ symmetry

$$\begin{aligned} \psi_1 &= C_1 \psi_{2s(C)} + C_2 \psi' && \text{(bonding)} \\ &= C_1 \psi_{2s(C)} + C_2 [\psi_{1s(H_1)} + \psi_{1s(H_2)} + \psi_{1s(H_3)} + \psi_{1s(H_4)}] && (5.18.44)^\dagger \end{aligned}$$

$$\begin{aligned} \psi_2 &= C'_1 \psi_{2s(C)} - C'_2 \psi' && \text{(antibonding)} \\ &= C'_1 \psi_{2s(C)} - C'_2 [\psi_{1s(H_1)} + \psi_{1s(H_2)} + \psi_{1s(H_3)} + \psi_{1s(H_4)}] && (5.18.45) \end{aligned}$$

### Molecular orbitals of $T_2$ symmetry

$$\begin{aligned} \psi_3 &= C_3 \psi_{2p_x(C)} + C_4 \psi_x && \text{(bonding)} \\ &= C_3 \psi_{2p_x(C)} + C_4 [\psi_{1s(H_1)} + \psi_{1s(H_2)} - \psi_{1s(H_3)} - \psi_{1s(H_4)}] && (5.18.46)^\dagger \end{aligned}$$

$$\begin{aligned} \psi_4 &= C'_3 \psi_{2p_x(C)} - C'_4 \psi_x && \text{(antibonding)} \\ &= C'_3 \psi_{2p_x(C)} - C'_4 [\psi_{1s(H_1)} + \psi_{1s(H_2)} - \psi_{1s(H_3)} - \psi_{1s(H_4)}] && (5.18.47) \end{aligned}$$

$$\begin{aligned} \psi_5 &= C_3 \psi_{2p_y(C)} + C_4 \psi_y && \text{(bonding)} \\ &= C_3 \psi_{2p_y(C)} + C_4 [\psi_{1s(H_1)} - \psi_{1s(H_2)} + \psi_{1s(H_3)} - \psi_{1s(H_4)}] && (5.18.48) \end{aligned}$$

$$\begin{aligned} \psi_6 &= C'_3 \psi_{2p_y(C)} - C'_4 \psi_y && \text{(antibonding)} \\ &= C'_3 \psi_{2p_y(C)} - C'_4 [\psi_{1s(H_1)} - \psi_{1s(H_2)} + \psi_{1s(H_3)} - \psi_{1s(H_4)}] && (5.18.49) \end{aligned}$$

$$\begin{aligned} \psi_7 &= C_3 \psi_{2p_z(C)} + C_4 \psi_z && \text{(bonding)} \\ &= C_3 \psi_{2p_z(C)} + C_4 [\psi_{1s(H_1)} - \psi_{1s(H_2)} - \psi_{1s(H_3)} + \psi_{1s(H_4)}] && (5.18.50) \end{aligned}$$

$$\begin{aligned} \psi_8 &= C'_3 \psi_{2p_z(C)} - C'_4 \psi_z && \text{(antibonding)} \\ &= C'_3 \psi_{2p_z(C)} - C'_4 [\psi_{1s(H_1)} - \psi_{1s(H_2)} - \psi_{1s(H_3)} + \psi_{1s(H_4)}] && (5.18.51) \end{aligned}$$

The molecular orbital  $\psi_1$  is bonding and build up charge between the carbon atom and each of the four hydrogen atoms. The molecular orbitals  $\psi_3$ ,  $\psi_5$  and  $\psi_7$  are bonding and build up charge in the regions about the  $x$ -,  $y$ - and  $z$ -axes, respectively.

<sup>†</sup> The values of  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  reported in literature are 0.58, 0.19, 0.55 and 0.32, respectively.

### Localized Bonding Molecular Orbitals of Methane

Because of the tetrahedral symmetry, each of the bonding molecular orbitals must point along a CH bond. The four localized bonding molecular orbitals may be obtained by the linear combination of four nonlocalized molecular orbitals  $\psi_1, \psi_2, \psi_3$  and  $\psi_4$ . We may write it as

$$\psi = a\psi_1 + b\psi_2 + c\psi_3 + d\psi_4 \quad (5.18.52)$$

The molecular orbital  $\psi_1$  is directed equally to all four hydrogen atoms, the variation in the value of  $a$  does not direct  $\psi$  preferentially to any one hydrogen. The molecular orbitals  $\psi_2, \psi_3$  and  $\psi_4$  are directed along the  $x, y$ - and  $z$ -axes, respectively, and thus the variations in  $b, c$  and  $d$  help directing  $\psi$  towards the hydrogen atoms.

Since  $\psi_2, \psi_3$  and  $\psi_4$  have directional characteristics along  $x, y$ - and  $z$ -axes, respectively, the linear combination of these orbitals in Eq. (5.18.52) will have directional characteristics of

$$bx + cy + dz \quad (5.18.53)$$

Let  $l_1, m_1$  and  $n_1$  be the direction cosines of the  $\text{CH}_4$  line (taken as the  $x'$  axis) with the original  $x, y$ - and  $z$ -axes, respectively. If the coefficients  $b, c$  and  $d$  are chosen as proportional to these direction cosines (i.e.  $b = el_1, c = em_1$  and  $d = en_1$ , where  $e$  is a constant of proportionality), then the direction as given by Eq. (5.18.53) is along the  $\text{CH}_4$  bond. We will have

$$bx + cy + dz = e(l_1x + m_1y + n_1z) = ex' \quad (5.18.54)$$

Since the above expression involves  $x'$ , the direction as given by Eq. (5.18.54) will be directed towards  $x'$ -axis (that is,  $\text{CH}_4$  line). With this, Eq. (5.18.52) becomes

$$\psi_{\text{CH}_4} = a\psi_1 + el_1\psi_2 + em_1\psi_3 + en_1\psi_4 \quad (5.18.55)$$

From Fig. (5.18.9), it follows that

$$l_1 = m_1 = n_1 = \cos (109^\circ 48' / 2) = 1/\sqrt{3}$$

$$\text{Hence } \psi_{\text{CH}_4} = a\psi_1 + (e/\sqrt{3})(\psi_2 + \psi_3 + \psi_4) \quad (5.18.56)$$

Proceeding similarly, it can be shown that

$$\psi_{\text{CH}_2} = a\psi_1 + (e/\sqrt{3})(\psi_2 - \psi_3 - \psi_4) \quad (5.18.57)$$

$$\psi_{\text{CH}_3} = a\psi_1 + (e/\sqrt{3})(-\psi_2 + \psi_3 - \psi_4) \quad (5.18.58)$$

$$\psi_{\text{CH}_4} = a\psi_1 + (e/\sqrt{3})(-\psi_2 - \psi_3 + \psi_4) \quad (5.18.59)$$

Orthonormality of the localized bonding molecular orbitals requires that

$$\frac{a^2}{3} + \frac{e^2}{3} + \frac{e^2}{3} = 1 \quad \text{i.e.} \quad a^2 + e^2 = 1$$

$$\frac{a^2}{3} - \frac{e^2}{3} - \frac{e^2}{3} = 0 \quad \text{i.e.} \quad a^2 - \frac{e^2}{3} = 0$$

### Explicit Expressions of Localized Molecular Orbitals

$$\text{These give } a = 1/2 \text{ and } e = \sqrt{3}/2. \quad (5.18.60)$$

With these, the expressions of localized molecular orbitals become

$$\psi_{\text{CH}_4} = \frac{1}{2}\psi_1 + \frac{1}{2}(\psi_2 + \psi_3 + \psi_4) \quad (5.18.61)$$

$$\psi_{\text{CH}_2} = \frac{1}{2}\psi_1 + \frac{1}{2}(\psi_2 - \psi_3 - \psi_4) \quad (5.18.62)$$

$$\psi_{\text{CH}_3} = \frac{1}{2}\psi_1 + \frac{1}{2}(-\psi_2 + \psi_3 - \psi_4) \quad (5.18.63)$$

$$\psi_{\text{CH}_4} = \frac{1}{2}\psi_1 + \frac{1}{2}(-\psi_2 - \psi_3 + \psi_4) \quad (5.18.64)$$

Substituting the expressions of  $\psi_1, \psi_2, \psi_3$  and  $\psi_4$ , we get

$$\begin{aligned} \psi_{\text{CH}_4} = & \frac{C_1}{2} \psi_{2s(\text{C})} + \frac{C_3}{2} [\psi_{2p_x(\text{C})} + \psi_{2p_y(\text{C})} + \psi_{2p_z(\text{C})}] + \left( \frac{C_2}{2} + \frac{3}{2} C_4 \right) \psi_{1s(\text{H}_a)} \\ & + \left( \frac{C_2}{2} - \frac{C_4}{2} \right) [\psi_{1s(\text{H}_b)} + \psi_{1s(\text{H}_c)} + \psi_{1s(\text{H}_d)}] \end{aligned}$$

The detail self-consistent-field calculations have shown that

$$C_1 = C_3 \quad \text{and} \quad C_2 = C_4$$

Setting  $C_1 = C_3$  and  $C_2 = C_4$ , the function  $\psi_{\text{CH}_4}$  becomes

$$\psi_{\text{CH}_4} = \frac{C_1}{2} [\psi_{2s(\text{C})} + \psi_{2p_x(\text{C})} + \psi_{2p_y(\text{C})} + \psi_{2p_z(\text{C})}] + 2C_2 \psi_{1s(\text{H}_a)} \quad (5.18.65)$$

Proceeding similarly, it can be shown that

$$\psi_{\text{CH}_2} = \frac{C_1}{2} [\psi_{2s(\text{C})} + \psi_{2p_x(\text{C})} - \psi_{2p_y(\text{C})} - \psi_{2p_z(\text{C})}] + 2C_2 \psi_{1s(\text{H}_b)} \quad (5.18.66)$$

$$\psi_{\text{CH}_3} = \frac{C_1}{2} [\psi_{2s(\text{C})} - \psi_{2p_x(\text{C})} + \psi_{2p_y(\text{C})} - \psi_{2p_z(\text{C})}] + 2C_2 \psi_{1s(\text{H}_c)} \quad (5.18.67)$$

$$\psi_{\text{CH}_4} = \frac{C_1}{2} [\psi_{2s(\text{C})} - \psi_{2p_x(\text{C})} - \psi_{2p_y(\text{C})} + \psi_{2p_z(\text{C})}] + 2C_2 \psi_{1s(\text{H}_d)} \quad (5.18.68)$$

The localized molecular orbitals include equal contributions from  $2s(\text{C})$ ,  $2p_x(\text{C})$ ,  $2p_y(\text{C})$  and  $2p_z(\text{C})$  orbitals, that is, the localized molecular orbitals include  $sp^3$  hybrid orbitals of carbon atom.

### Correlation Diagram of $\text{CH}_4$

The correlation diagrams depicting nonlocalized and localized molecular orbitals of  $\text{CH}_4$  are shown in Fig. 5.18.10.

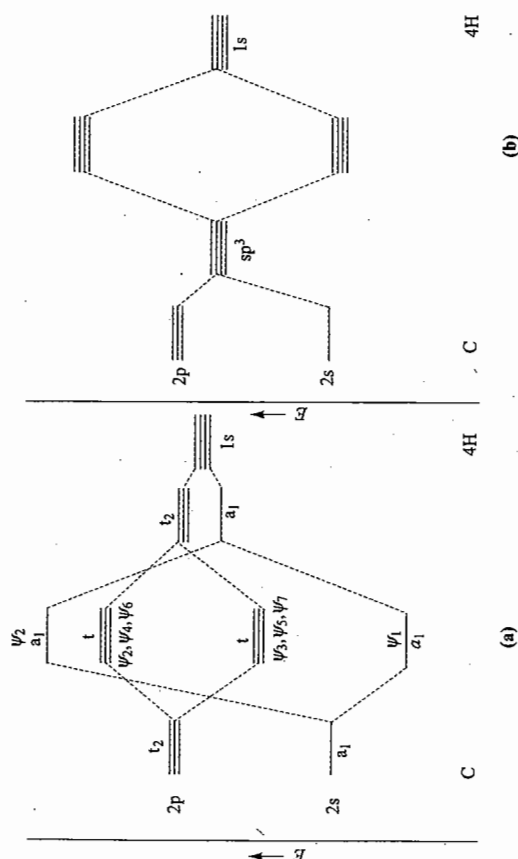


Fig. 5.18.10 Correlation diagrams depicting (a) nonlocalized and (b) localized molecular orbitals of  $\text{CH}_4$ .

### SALC's AND $\pi$ -MOLECULAR ORBITALS OF *trans*-BUTADIENE

The point group of *trans*-butadiene (Fig. 5.18.8) is  $C_{2h}$ .

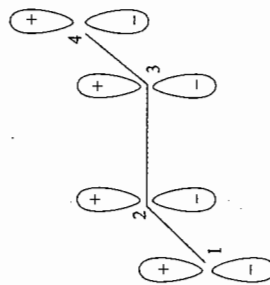


Fig. 5.18.8 Four  $2p_z$  orbitals of *trans*-butadiene

### Nature of Irreducible Representations

The reducible representation based on the four  $2p_z$  orbitals (which point in the direction perpendicular to molecular plane) is

$C_{2h}$	$E$	$C_2$	$i$	$\sigma_h$	
$\Gamma_\pi$	4	0	0	-4	
	(All the four orbitals remain unshifted)	(All the four orbitals are shifted)	(All the four orbitals are reversed)	(All the four orbitals are reversed without shifting)	

The use of reduction formula  $a_i = (1/h_i) \sum_R \chi(R) \chi_i(R)$  gives

$$a(A_g) = \frac{1}{4} [(4)(1) + (0)(1) + (0)(1) + (-4)(1)] = 0$$

$$a(B_g) = \frac{1}{4} [(4)(1) + (0)(-1) + (0)(1) + (-4)(-1)] = 2$$

$$a(A_u) = \frac{1}{4} [(4)(1) + (0)(1) + (0)(-1) + (-4)(-1)] = 2$$

$$a(B_u) = \frac{1}{4} [4(1) + (0)(-1) + (0)(-1) + (-4)(1)] = 0$$

Hence,  $\Gamma_\pi = 2B_g + 2A_u$  (5.18.69)

### SALC from $2p_z$ Orbitals of Carbon Atoms

The four  $2p_z$  orbitals form two subsets,  $\phi_1$  and  $\phi_4$ , and  $\phi_2$  and  $\phi_3$ , respectively. The members of each are symmetry equivalent to each other but not to those in other sets. We construct molecular orbitals taking one from each subset,

- The use of projection operator ( $\hat{P}_j = \sum_R \chi_j(R) \hat{R}$ ) on the  $2p_z$  orbitals of carbons 1 and 2 (represented respectively by  $\phi_1$  and  $\phi_2$ ), we get

$$\begin{aligned} \hat{P}_{B_g} \phi_1 &= \chi_{B_g}(E) \{ \hat{E} \phi_1 \} + \chi_{B_g}(C_2) \{ \hat{C}_2 \phi_1 \} + \chi_{B_g}(i) \{ \hat{i} \phi_1 \} + \chi_{B_g}(\sigma_h) \{ \hat{\sigma}_h \phi_1 \} \\ &= (1)(\phi_1) + (-1) \phi_4 + (1)(-\phi_4) + (-1)(-\phi_1) \\ &= 2(\phi_1 - \phi_4) \end{aligned} \quad (5.18.70)$$

Similarly, we will have

$$\hat{P}_{B_g} \phi_2 = 2(\phi_2 - \phi_3) \quad (5.18.71)$$

$$\hat{P}_{A_u} \phi_1 = 2(\phi_1 + \phi_4) \quad (5.18.72)$$

$$\hat{P}_{A_u} \phi_2 = 2(\phi_2 + \phi_3) \quad (5.18.73)$$

The interactions between the two  $B_g$  combinations and the two  $A_u$  combinations give the following four molecular orbitals of *trans*-butadiene

$$B_g: \psi_1 = a_1(\phi_1 - \phi_4) + a_2(\phi_2 - \phi_3) \quad (5.18.74)$$

$$\psi_2 = a_2(\phi_1 - \phi_4) - a_1(\phi_2 - \phi_3) \quad (5.18.75)$$

$$A_u: \psi_3 = a_3(\phi_1 + \phi_4) + a_4(\phi_2 + \phi_3) \quad (5.18.76)$$

$$\psi_4 = a_4(\phi_1 + \phi_4) - a_3(\phi_2 + \phi_3) \quad (5.18.77)$$

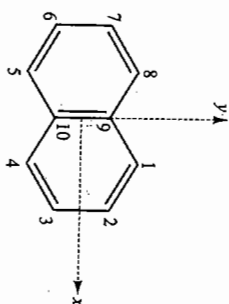
where  $a_1, a_2, a_3$  and  $a_4$  are constants. The detail quantum-mechanical calculations† result into

$$a_1 = a_4 = 0.602 \text{ and } a_2 = a_3 = 0.372.$$

† See Section 5.21

**$\pi$ -MOLECULAR ORBITALS OF NAPHTHALENE**The point group of naphthalene (Fig. 5.18.9) is  $D_{2h}$ .**Nature of Irreducible Representations**

Fig. 18.9

Naphthalene molecule. The  $z$ -direction is perpendicular to the plane of moleculeThe reducible representation obtained on the basis of ten  $2p_z$  orbitals (which point in the direction perpendicular to molecular plane) is

$D_{2h}$	$E$	$C_2(z)$	$C_2(y)$	$C_2(x)$	$i$	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_\pi$	10	0	-2	0	0	-10	0	2
	All the ten orbitals remain unshifted	All orbitals are shifted	Eight orbitals are shifted. Two orbitals of $C_9$ and $C_{10}$ undergo reversal in direction	All the ten orbitals are shifted	All the ten orbitals undergo reversal in direction	All the ten orbitals are shifted	All the ten orbitals are shifted	Eight orbitals are shifted. Two orbitals of $C_9$ and $C_{10}$ remain unshifted

The use of reduction formula [ $a_i = (1/h_i) \sum_R \chi(R) \chi_i(R)$ ] gives

$$a(A_g) = \frac{1}{8} [(10)(1) + (-2)(1) + (-10)(1) + (2)(1)] = 0$$

$$a(B_{1g}) = \frac{1}{8} [(10)(1) + (-2)(-1) + (-10)(1) + (2)(-1)] = 0$$

$$a(B_{2g}) = \frac{1}{8} [(10)(1) + (-2)(1) + (-10)(-1) + (2)(-1)] = 2$$

$$a(B_{3g}) = \frac{1}{8} [(10)(1) + (-2)(-1) + (-10)(-1) + (2)(1)] = 3$$

$$a(A_u) = \frac{1}{8} [(10)(1) + (-2)(1) + (-10)(-1) + (2)(-1)] = 2$$

$$a(B_{1u}) = \frac{1}{8} [(10)(1) + (-2)(-1) + (-10)(-1) + (2)(1)] = 3$$

$$a(B_{2u}) = \frac{1}{8} [(10)(1) + (-2)(1) + (-10)(1) + (2)(1)] = 0$$

$$a(B_{3u}) = \frac{1}{8} [(10)(1) + (-2)(-1) + (-10)(1) + (2)(-1)] = 0$$

**SALC from  $2p_z$  Orbitals of Carbon Atoms**

$$\text{Hence } \Gamma_\pi = 2B_{2g} + 3B_{3g} + 2A_u + 3B_{1u} \quad (5.18.78)$$

The ten  $2p_z$  orbitals form three subsets:Subset 1:  $\phi_1, \phi_4, \phi_5, \phi_8$ Subset 2:  $\phi_2, \phi_3, \phi_6, \phi_7$ Subset 3:  $\phi_9$  and  $\phi_{10}$ 

The members in each subset are symmetry-equivalent to each other but not to those in other sets. We construct the required number of symmetry-adapted linear combination of given symmetry taking one orbital from each subset. For example, for two  $B_{2g}$  molecular orbitals, and we apply projection operator on the orbital  $\phi_1$  (subset 1) and  $\phi_2$  (subset 2), respectively, and so on.

$$B_{2g}: \hat{P}_{B_{2g}} \phi_1 = [\chi(E)\{\hat{E}\phi_1\} + \chi(C_{2z})\{\hat{C}_{2z}\phi_1\} + \chi(C_{2y})\{\hat{C}_{2y}\phi_1\}$$

$$+ \chi(C_{2x})\{\hat{C}_{2x}\phi_1\} + \chi(i)\{\hat{i}\phi_1\} + \chi(\sigma_{xy})\{\hat{\sigma}_{xy}\phi_1\} \\ + \chi(\sigma_{xz})\{\hat{\sigma}_{xz}\phi_1\} + \chi(\sigma_{yz})\{\hat{\sigma}_{yz}\phi_1\}] \\ = [(1)\phi_1 + (-1)\phi_5 + (1)(-\phi_8) + (-1)(-\phi_4) \\ + (1)(-\phi_2) + (-1)(-\phi_7) + (1)(\phi_3) + (-1)(\phi_6)]$$

$$\text{i.e. } \psi'_1 = 2[\phi_1 - \phi_5 - \phi_8 + \phi_4]$$

$$\text{The normalized SALC is } \psi'_1 = \frac{1}{2} [\phi_1 - \phi_5 - \phi_8 + \phi_4] \quad (5.18.79)$$

$$\hat{P}_{B_{2g}} \phi_2 = [(1)\phi_2 + (-1)\phi_6 + (1)(-\phi_7) + (-1)(-\phi_3) \\ + (1)(-\phi_4) + (-1)(-\phi_2) + (1)(\phi_3) + (-1)(\phi_7)]$$

$$\text{i.e. } \psi'_2 = 2[\phi_2 - \phi_6 - \phi_7 + \phi_3]$$

$$\text{The normalized SALC is } \psi'_2 = \frac{1}{2} [\phi_2 - \phi_6 - \phi_7 + \phi_3] \quad (5.18.80)$$

$$B_{3g}: \hat{P}_{B_{3g}} \phi_1 = [(1)\phi_1 + (-1)\phi_5 + (-1)(-\phi_8) + (1)(-\phi_4) \\ + (1)(-\phi_2) + (-1)(-\phi_7) + (-1)(\phi_3) + (1)(\phi_6)]$$

$$\text{i.e. } \psi'_3 = 2[\phi_1 - \phi_5 + \phi_8 - \phi_4]$$

$$\text{The normalized SALC is } \psi'_3 = \frac{1}{2} [\phi_1 - \phi_5 + \phi_8 - \phi_4] \quad (5.18.81)$$

$$\hat{P}_{B_{3g}} \phi_2 = [(1)\phi_2 + (-1)\phi_6 + (-1)(-\phi_7) + (1)(-\phi_3) \\ + (1)(-\phi_4) + (-1)(-\phi_2) + (-1)(\phi_3) + (1)(\phi_7)]$$

$$\text{i.e. } \psi'_4 = 2[\phi_2 - \phi_6 + \phi_7 - \phi_3]$$



The normalized SALC is  $\psi'_4 = \frac{1}{2}(\varphi_2 - \varphi_6 + \varphi_7 - \varphi_3)$  (5.18.82)

$$\hat{P}_{B_{3g}} \varphi_9 = [(1)\varphi_9 + (-1)(\varphi_{10}) + (-1)(-\varphi_9) + (1)(-\varphi_{10}) \\ + (1)(-\varphi_{10}) + (-1)(-\varphi_9) + (-1)(\varphi_{10}) + (1)\varphi_9] \\ \text{i.e. } \psi'_5 = 4[\varphi_9 - \varphi_{10}]$$

The normalized SALC is  $\psi'_5 = \frac{1}{\sqrt{2}}(\varphi_9 - \varphi_{10})$  (5.18.83)

$$\hat{P}_{A_u} \varphi_1 = [(1)\varphi_1 + (1)\varphi_5 + (1)(-\varphi_8) + (1)(-\varphi_4) \\ + (-1)(-\varphi_3) + (-1)(-\varphi_1) + (-1)\varphi_4 + (-1)\varphi_8] \\ \text{i.e. } \psi'_6 = 2[\varphi_1 + \varphi_5 - \varphi_8 - \varphi_4]$$

The normalized SALC is  $\psi'_6 = \frac{1}{2}(\varphi_1 + \varphi_5 - \varphi_8 - \varphi_4)$  (5.18.84)

$$\hat{P}_{A_u}(\varphi_2) = [(1)\varphi_2 + (1)\varphi_6 + (1)(-\varphi_7) + (1)(-\varphi_3) \\ + (-1)(-\varphi_6) + (-1)(-\varphi_2) + (-1)\varphi_3 + (-1)\varphi_7] \\ \text{i.e. } \psi'_7 = 2[\varphi_2 + \varphi_6 - \varphi_7 - \varphi_3]$$

The normalized SALC is  $\psi'_7 = \frac{1}{2}(\varphi_2 + \varphi_6 - \varphi_7 - \varphi_3)$  (5.18.85)

$$\hat{P}_{B_{1u}} \varphi_1 = [(1)\varphi_1 + (1)\varphi_5 + (-1)(-\varphi_8) + (-1)(-\varphi_4) \\ + (-1)(-\varphi_5) + (-1)(-\varphi_1) + (1)\varphi_4 + (1)\varphi_8] \\ \text{i.e. } \psi'_8 = 2[\varphi_1 + \varphi_5 + \varphi_8 + \varphi_4]$$

The normalized SALC is  $\psi'_8 = \frac{1}{2}(\varphi_1 + \varphi_5 + \varphi_8 + \varphi_4)$  (5.18.86)

$$\hat{P}_{B_{1u}}(\varphi_2) = [(1)\varphi_2 + (1)\varphi_6 + (-1)(-\varphi_7) + (-1)(-\varphi_3) \\ + (-1)(-\varphi_6) + (-1)(-\varphi_2) + (1)\varphi_3 + (1)\varphi_7] \\ \text{i.e. } \psi'_9 = 2[\varphi_2 + \varphi_6 + \varphi_7 + \varphi_3]$$

The normalized SALC is  $\psi'_9 = \frac{1}{2}(\varphi_2 + \varphi_6 + \varphi_7 + \varphi_3)$  (5.18.87)

$$\hat{P}_{B_{1u}}(\varphi_9) = [(1)\varphi_9 + (1)\varphi_{10} + (-1)(-\varphi_9) + (-1)(-\varphi_{10}) \\ + (-1)(-\varphi_{10}) + (-1)(-\varphi_9) + (1)\varphi_{10} + (1)\varphi_9] \\ \text{i.e. } \psi'_{10} = 4[\varphi_9 + \varphi_{10}]$$

The normalized SALC is  $\psi'_{10} = \frac{1}{\sqrt{2}}(\varphi_9 + \varphi_{10})$  (5.18.88)

The SALC's  $\psi'_1, \psi'_2, \dots, \psi'_{10}$  may be combined to give molecular orbitals of naphthalene. Since the combinations of the same symmetry combine, we form molecular orbitals as listed in the following.

MO's of  
Naphthalene

## 5.19 $\pi$ -MOLECULAR ORBITALS OF A CARBOCYCLIC SYSTEM

### Carbocyclic System

The molecular formula of carbocyclic systems is  $C_nH_n$ . Each carbon atom of a carbocyclic molecule carries a  $\pi$ -electron in its  $p_z$  orbital which is in the perpendicular direction of the molecular plane. Examples include  $C_3H_3$ ,  $C_4H_4$ ,  $C_5H_5$ ,  $C_6H_6$  and so on. The SALC involving  $p_z$  orbitals of carbon atoms of a carbocyclic molecule can be easily constructed by using the pure rotational symmetry about the principal axis of the molecule and by using the characters from the character table of the cyclic group.

A cyclic group of order  $h$  is defined by elements  $X^n$ , where  $n = 1, 2, \dots, h$  with  $X^h = E$ . Each of its  $h$  elements constitutes a separate class. Thus, it has  $h$  one-dimensional irreducible representations. Since  $X^m X^n = X^n X^m$ , a cyclic group is an Abelian group.

### Irreducible Representations of a Cyclic Group

A general scheme to write irreducible representations of a cyclic group is available. This is based on the use of exponential

$$\varepsilon_h = \exp(2\pi i/h) \quad \text{Obviously,} \quad (5.19.1)$$

$$\varepsilon_h^h = [\exp(2\pi i/h)]^h = \exp(2\pi i) = \exp(2\pi) \\ = \cos 2\pi + i \sin 2\pi = 1 + 0 = 1$$

In terms of  $\varepsilon_h$ , the irreducible representations of a cyclic group of  $h = 5$  are shown in Table 5.19.1.

Table 5.19.1 Irreducible Representations of Cyclic Group of Order 5

	$C_5$	$C_5^2$	$C_5^3$	$C_5^4$	$C_5^5$
$\Gamma_1$	$\varepsilon_5$	$\varepsilon_5^2$	$\varepsilon_5^3$	$\varepsilon_5^4$	$\varepsilon_5^5$
$\Gamma_2 = (\Gamma_1)^2$	$\varepsilon_5^2$	$\varepsilon_5^4$	$\varepsilon_5^6$	$\varepsilon_5^8$	$\varepsilon_5^{10}$
$\Gamma_3 = (\Gamma_1)^3$	$\varepsilon_5^3$	$\varepsilon_5^6$	$\varepsilon_5^9$	$\varepsilon_5^{12}$	$\varepsilon_5^{15}$
$\Gamma_4 = (\Gamma_1)^4$	$\varepsilon_5^4$	$\varepsilon_5^8$	$\varepsilon_5^{12}$	$\varepsilon_5^{16}$	$\varepsilon_5^{20}$
$\Gamma_5 = (\Gamma_1)^5$	$\varepsilon_5^5$	$\varepsilon_5^{10}$	$\varepsilon_5^{15}$	$\varepsilon_5^{20}$	$\varepsilon_5^{25}$

**Rewriting Table 5.19.1**

The representations given in Table 5.19.1 constitute a orthonormal set satisfying the expression

$$\sum_{n=1}^h [\Gamma_p(C_h^n)]^* [\Gamma_q(C_h^n)] = \delta_{pq} \quad h \quad (5.19.2)$$

The representations shown in Table 5.19.1 can be written with smaller exponents using the following facts:

$$C_h^h = E$$

$$C_h^{nh} = C_h^h \quad C_h^h \dots n \text{ times} = (1) \quad (1) \dots = 1$$

$$\text{and} \quad C_h^m = C_h^{n+h} = C_h^n \quad C_h^h = C_h^n \text{ with } m > h \text{ and } n < h. \quad (5.19.3)$$

The resultant representations are shown in Table 5.19.2.

**Table 5.19.2 Representations of the Cyclic Group of Order Five**

	$C_5$	$C_5^2$	$C_5^3$	$C_5^4$	$C_5^5$
$\Gamma_1$	$\epsilon_5$	$\epsilon_5^2$	$\epsilon_5^3$	$\epsilon_5^4$	1
$\Gamma_2$	$\epsilon_5^2$	$\epsilon_5^4$	$\epsilon_5$	$\epsilon_5^3$	1
$\Gamma_3$	$\epsilon_5^3$	$\epsilon_5$	$\epsilon_5^4$	$\epsilon_5^2$	1
$\Gamma_4$	$\epsilon_5^4$	$\epsilon_5$	$\epsilon_5^2$	$\epsilon_5$	1
$\Gamma_5$	1	1	1	1	1

Also from the fact that

$$\begin{aligned} [e_h^n]^* &= \left[ \cos \frac{2\pi n}{h} + i \sin \frac{2\pi n}{h} \right]^* = \cos \frac{2\pi n}{h} - i \sin \frac{2\pi n}{h} \\ &= \cos \left\{ 2\pi - \frac{2\pi n}{h} \right\} + i \sin \left\{ 2\pi - \frac{2\pi n}{h} \right\} \\ &= \cos \frac{2\pi(h-n)}{h} + i \sin \frac{2\pi(h-n)}{h} \\ &= e_h^{(h-n)} \quad (5.19.4) \end{aligned}$$

we can write the representations of Table 5.19.2 as shown in Table 5.19.3.

**Table 5.19.3 Representations of Cyclic Group of Order Five**

	$C_5$	$C_5^2$	$C_5^3$	$C_5^4$	$C_5^5$
$\Gamma_1$	$\epsilon_5$	$\epsilon_5^2$	$\epsilon_5^3$	$\epsilon_5^4$	1
$\Gamma_2$	$\epsilon_5^2$	$\epsilon_5^4$	$\epsilon_5$	$\epsilon_5^3$	1
$\Gamma_3$	$\epsilon_5^3$	$\epsilon_5$	$\epsilon_5^4$	$\epsilon_5^2$	1
$\Gamma_4$	$\epsilon_5^4$	$\epsilon_5$	$\epsilon_5^2$	$\epsilon_5$	1
$\Gamma_5$	1	1	1	1	1

**Rearrangement Table 5.19.3****Table 5.19.4 Character Table of Cyclic Group of Order Five**

	$E$	$C_5$	$C_5^2$	$C_5^3$	$C_5^4$
$A$	1	1	1	1	1
$E_1$	1	$\epsilon_5$	$\epsilon_5^2$	$\epsilon_5^3$	$\epsilon_5^4$
$E_2$	1	$\epsilon_5^4$	$\epsilon_5^3$	$\epsilon_5^2$	$\epsilon_5$

In Table 5.19.4, the E representations appear in the form of two associated one-dimensional representations. The use of corresponding projection operator provide the two symmetry-adapted linear combinations belonging to the E representation. This is advantage of using only the principal axis rotational symmetry for constructing molecular orbitals.

The rule states that

In a cyclic  $(CH)_n$  molecule with rotational symmetry  $C_n$ , there will always be  $n$   $\pi$  molecular orbitals, one-belonging to each irreducible representation of the group  $C_n$ . The above rule may be illustrated by taking an example of benzene ( $C_6H_6$ ).

The reducible representation of benzene based on six  $p_z$  orbitals is as follows.

$\Gamma_\pi$	$E$	$C_6$	$C_6^2 = C_3$	$C_6^3 = C_2$	$C_6^4 = C_3^2$	$C_6^5$
	6	0	0	0	0	0

Note that  $\chi(E) = 6$  and all other characters are zero. This follows from the fact that only the identity operation leaves each of  $p_z$  orbital unshifted while all other operations shift each of  $p_z$  orbitals.

The character table of  $C_6$  group is as follows.

	$E$	$C_6$	$C_3$	$C_2$	$C_3^2$	$C_6^5$
$A$	1	1	1	1	1	1
$B$	1	-1	1	-1	1	-1
$E_1$	1	$\epsilon_6$	$\epsilon_6^2$	$\epsilon_6^4$	$\epsilon_6^3$	$\epsilon_6$
$E_2$	1	$\epsilon_6^5$	$\epsilon_6^4$	$\epsilon_6^2$	$\epsilon_6$	$\epsilon_6^3$

<sup>†</sup> In the new rearrangement, we have

- The total symmetric representation is written at the top. It is represented by the symbol A.
- The remaining representations are written in pairs, such that the elements of one row in each pair are complex conjugate of the other.

If the reducible representation listed above is resolved into irreducible representations, we find that

$$\Gamma_{\pi} = A + B + E_1 + E_2$$

The above result follows from the fact that the only way to get  $\chi(E) = 6$  and all other characters zero is that the sum of characters of various irreducible representations in a symmetry operation is always zero except that of E operation.

Thus, each of the six molecular orbitals of  $C_6H_6$  molecule belongs to each of the six irreducible representations of the group  $C_6$ .

Since each of the six linear combinations belongs to separate one-dimensional representation, the projection operator technique is extremely simple to apply. The result is the expression which includes the sum of six terms involving the product  $p_z$  orbital taken in numerical order with the character for one of the six operations in the conventional order (for example,  $E, C_6, C_6^2, C_6^3, \dots$ ). Hence, the sets of characters of the group are the coefficients of the LCAO-MO's.

To illustrate the above fact, we built molecular orbital of  $C_6H_6$  molecule belonging to  $E_1$  representation. The use of projection operator gives

$$\begin{aligned}\hat{P}_{E_1}\phi_1 &= \chi(E)\hat{E}\phi_1 + \chi(C_6)\hat{C}_6\phi_1 + \chi(C_6^2)\hat{C}_6^2\phi_1 + \chi(C_6^3)\hat{C}_6^3\phi_1 \\ &\quad + \chi(C_6^4)\hat{C}_6^4\phi_1 + \chi(C_6^5)\hat{C}_6^5\phi_1 \\ &= \chi(E)\phi_1 + \chi(C_6)\phi_2 + \chi(C_6^2)\phi_3 + \chi(C_6^3)\phi_4 + \chi(C_6^4)\phi_5 + \chi(C_6^5)\phi_6\end{aligned}$$

### $\pi$ -MOLECULAR ORBITALS OF THE CYCLOPROPENYL

The cyclopropenyl has a molecular formula  $C_3H_3$ . Each carbon has one  $\pi$ -electron in the respective  $p_z$  orbital (Fig. 5.19.1)

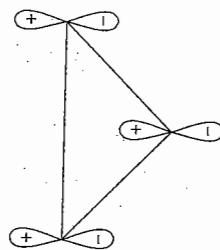


Fig. 5.19.1  $\pi$ -Orbitals of cyclopropenyl

The symmetry-adapted linear combination of the three  $p_z$  orbitals can be constructed by using the character table for the cyclic system of order  $h = 3$  (Table 5.19.5).

Table 5.19.5 Character Table of Cyclic System of Order  $h = 3$

	$C_3$	$E$	$C_3$	$C_3^2$
A	1	1	1	1
E	$\begin{Bmatrix} 1 & \epsilon_3 & \epsilon_3^* \\ 1 & \epsilon_3^* & \epsilon_3 \end{Bmatrix}$	$\begin{Bmatrix} 1 & \epsilon_3 & \epsilon_3^* \\ 1 & \epsilon_3^* & \epsilon_3 \end{Bmatrix}$	$\begin{Bmatrix} 1 & \epsilon_3 & \epsilon_3^* \\ 1 & \epsilon_3^* & \epsilon_3 \end{Bmatrix}$	$\begin{Bmatrix} 1 & \epsilon_3 & \epsilon_3^* \\ 1 & \epsilon_3^* & \epsilon_3 \end{Bmatrix}$ (where $\epsilon_3 = \exp(2\pi i/3)$ )

Application of the projection operators  $\hat{P}_A, \hat{P}_{E(1)}$  and  $\hat{P}_{E(2)}$  to the orbital  $\phi$  (neglecting constant numerical factors) gives the following molecular orbitals.

$$\begin{aligned}\hat{P}_A\phi_1 &= \{\chi_A(E)\}\hat{E}\phi_1 + \{\chi_A(C_3)\}\hat{C}_3\phi_1 + \{\chi_A(C_3^2)\}\hat{C}_3^2\phi_1 \\ &= (1)\phi_1 + (1)\phi_2 + (1)\phi_3\end{aligned}$$

$$\text{i.e. } \psi_1 = \phi_1 + \phi_2 + \phi_3 \quad (5.19.5)$$

$$\begin{aligned}\hat{P}_{E(1)}\phi_1 &= \{\chi_{E(1)}(E)\}\hat{E}\phi_1 + \{\chi_{E(1)}(C_3)\}\hat{C}_3\phi_1 + \{\chi_{E(1)}(C_3^2)\}\hat{C}_3^2\phi_1 \\ &= (1)\phi_1 + (\epsilon_3)\phi_2 + (\epsilon_3^*)\phi_3\end{aligned}$$

$$\text{i.e. } \psi'_2 = \phi_1 + \epsilon_3\phi_2 + \epsilon_3^*\phi_3 \quad (5.19.6)$$

$$\begin{aligned}\hat{P}_{E(2)}\phi_1 &= \{\chi_{E(2)}(E)\}\hat{E}\phi_1 + \{\chi_{E(2)}(C_3)\}\hat{C}_3\phi_1 + \{\chi_{E(2)}(C_3^2)\}\hat{C}_3^2\phi_1 \\ &= (1)\phi_1 + (\epsilon_3^*)\phi_2 + (\epsilon_3)\phi_3\end{aligned}$$

$$\text{i.e. } \psi'_3 = \phi_1 + \epsilon_3^*\phi_2 + \epsilon_3\phi_3 \quad (5.19.7)$$

The combinations  $\psi'_2$  and  $\psi'_3$  involve imaginary coefficients. To write the combinations involving real coefficients, we take the following linear combinations

$$\psi_2 = \psi'_2 + \psi'_3 \quad (5.19.8)$$

$$\psi_3 = \frac{1}{i}[\psi'_2 - \psi'_3] \quad (5.19.9)$$

Thus, we get

$$\begin{aligned}\psi_2 &= [\phi_1 + \epsilon_3\phi_2 + \epsilon_3^*\phi_3] + [\phi_1 + \epsilon_3^*\phi_2 + \epsilon_3\phi_3] \\ &= 2\phi_1 + (\epsilon_3 + \epsilon_3^*)\phi_2 + (\epsilon_3 + \epsilon_3^*)\phi_3\end{aligned}$$

$$\text{Since } \epsilon_3 = \exp(2\pi i/3) = \cos(2\pi/3) + i \sin(2\pi/3)$$

$$\text{and } \epsilon_3^* = \exp(-2\pi i/3) = \cos(2\pi/3) - i \sin(2\pi/3)$$

$$\text{we get } \psi_2 = 2\phi_1 + \{2 \cos(2\pi/3)\}\phi_2 + \{2 \cos(2\pi/3)\}\phi_3$$

$$= 2\phi_1 - \phi_2 - \phi_3 \quad (5.19.10)$$

$$\psi_3 = \frac{1}{i}[\psi'_2 - \psi'_3] = \frac{1}{i}[(\epsilon_3\phi_2 + \epsilon_3^*\phi_3) - (\epsilon_3^*\phi_2 + \epsilon_3\phi_3)]$$

$$= \frac{1}{i}[(\epsilon_3 - \epsilon_3^*)\phi_2 + (\epsilon_3^* - \epsilon_3)\phi_3]$$

$$= \frac{1}{i}[\{2i \sin(2\pi/3)\}\phi_2 + \{-2i \sin(2\pi/3)\}\phi_3]$$

$$= \sqrt{3}(\phi_2 - \phi_3) \quad (5.19.11)$$

The three normalized combinations are

$$\psi_1^{(A)} = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3) \quad (5.19.12)$$

$$\psi_2^{(E)} = \frac{1}{\sqrt{6}}(2\phi_1 + \phi_2 - \phi_3) \quad (5.19.13)$$

$$\psi_3^{(E)} = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) \quad (5.19.14)$$

### $\pi$ -MOLECULAR ORBITALS OF BENZENE

Benzene is a carbocyclic system. The cyclic group of order  $h = 6$  (see, page 623) can be used to built six  $\pi$ -molecular orbitals (Fig. 5.19.2).

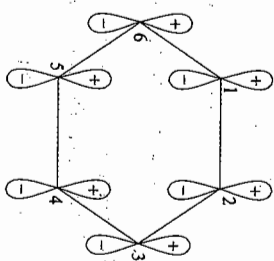


Fig. 5.19.2 Benzene Molecule

$$\hat{P}_A \phi_1 = [\chi_A(E)] \hat{E} \phi_1 + [\chi_A(C_6)] \hat{C}_6 \phi_1 + [\chi_A(C_3^2)] \hat{C}_6^2 \phi_1$$

$$+ [\chi_A(C_3)] \hat{C}_6^3 \phi_1 + [\chi_A(C_2^2)] \hat{C}_6^4 \phi_1 + [\chi_A(C_2)] \hat{C}_6^5 \phi_1$$

$$= (1)\phi_1 + (1)\phi_2 + (1)\phi_3 + (1)\phi_4 + (1)\phi_5 + (1)\phi_6$$

$$\text{Hence, } \psi_1 = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 \quad (5.19.15)$$

$$\hat{P}_B \phi_1 = (1)\phi_1 + (-1)\phi_2 + (1)\phi_3 + (-1)\phi_4 + (1)\phi_5 + (-1)\phi_6$$

$$\text{Hence, } \psi_2 = \phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6 \quad (5.19.16)$$

$$\hat{P}_{E_1(1)} \phi_1 = (1)\phi_1 + (\epsilon_6)\phi_2 + (-\epsilon_6^*)\phi_3 + (-1)\phi_4 + (-\epsilon_6)\phi_5 + (\epsilon_6^*)\phi_6$$

$$\text{Hence, } \psi_3 = \phi_1 + \epsilon_6\phi_2 - \epsilon_6^*\phi_3 - \phi_4 - \epsilon_6\phi_5 + \epsilon_6^*\phi_6 \quad (5.19.17)$$

$$\hat{P}_{E_1(2)} \phi_1 = (1)\phi_1 + (\epsilon_6^*)\phi_2 + (-\epsilon_6)\phi_3 + (-1)\phi_4 + (-\epsilon_6^*)\phi_5 + (\epsilon_6)\phi_6$$

$$\text{Hence, } \psi_4 = \phi_1 + \epsilon_6^*\phi_2 - \epsilon_6\phi_3 - \phi_4 - \epsilon_6^*\phi_5 + \epsilon_6\phi_6 \quad (5.19.18)$$

$$\hat{P}_{E_2(1)} \phi_1 = (1)\phi_1 + (-\epsilon_6^*)\phi_2 + (-\epsilon_6)\phi_3 + (1)\phi_4 + (-\epsilon_6^*)\phi_5 + (-\epsilon_6)\phi_6$$

$$\text{Hence, } \psi_5 = \phi_1 - \epsilon_6^*\phi_2 - \epsilon_6\phi_3 + \phi_4 - \epsilon_6^*\phi_5 - \epsilon_6\phi_6 \quad (5.19.19)$$

$$\hat{P}_{E_2(2)} \phi_1 = (1)\phi_1 + (-\epsilon_6)\phi_2 + (-\epsilon_6^*)\phi_3 + (1)\phi_4 + (-\epsilon_6^*)\phi_5 + (-\epsilon_6)\phi_6$$

$$\text{Hence } \psi_6 = \phi_1 - \epsilon_6\phi_2 - \epsilon_6^*\phi_3 + \phi_4 - \epsilon_6\phi_5 - \epsilon_6^*\phi_6 \quad (5.19.20)$$

The molecular orbitals involving real coefficients are obtained as follows.

$$\psi_3 = \psi_3' + \psi_4' = 2\phi_1 + (\epsilon_6 + \epsilon_6^*)\phi_2 - (\epsilon_6^* + \epsilon_6)\phi_3 - 2\phi_4 - (\epsilon_6 + \epsilon_6^*)\phi_5$$

$$+ (\epsilon_6 + \epsilon_6^*)\phi_6$$

$$= 2\phi_1 + 2\cos(2\pi/6)\phi_2 - 2\cos(2\pi/6)\phi_3 - 2\phi_4 - 2\cos(2\pi/6)\phi_5 + 2\cos(2\pi/6)\phi_6$$

$$= 2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6 \quad (5.19.21)$$

$$\psi_4 = \frac{\psi_3 - \psi_4'}{2} = \frac{1}{2}[(\epsilon_6 - \epsilon_6^*)\phi_2 + (\epsilon_6 - \epsilon_6^*)\phi_3 - (\epsilon_6 - \epsilon_6^*)\phi_5 - (\epsilon_6 - \epsilon_6^*)\phi_6]$$

$$= \frac{1}{2}[2i \sin(2\pi/6)\phi_2 + 2i \sin(2\pi/6)\phi_3 - 2i \sin(2\pi/6)\phi_5 - 2i \sin(2\pi/6)\phi_6]$$

$$= \sqrt{3}[\phi_2 + \phi_3 - \phi_5 - \phi_6] \quad (5.19.22)$$

$$\psi_5 = \psi_5' + \psi_6' = 2\phi_1 - (\epsilon_6 + \epsilon_6^*)\phi_2 - (\epsilon_6 + \epsilon_6^*)\phi_3 + 2\phi_4 - (\epsilon_6 + \epsilon_6^*)\phi_5 - (\epsilon_6 + \epsilon_6^*)\phi_6$$

$$= 2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6 \quad (5.19.23)$$

$$\psi_6 = \frac{\psi_5 - \psi_6'}{2} = \frac{1}{2}[(\epsilon_6 - \epsilon_6^*)\phi_2 - (\epsilon_6 - \epsilon_6^*)\phi_3 + (\epsilon_6 - \epsilon_6^*)\phi_5 - (\epsilon_6 - \epsilon_6^*)\phi_6]$$

$$= \phi_2 - \phi_3 + \phi_5 - \phi_6 \quad (5.19.24)$$

Finally, the molecular orbitals are normalized to give

$$\psi_1(A) = \frac{1}{\sqrt{6}}[\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6] \quad (5.19.25)$$

$$\psi_2(B) = \frac{1}{\sqrt{6}}[\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6] \quad (5.19.26)$$

$$\psi_3(E_1) = \frac{1}{\sqrt{12}}[\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6] \quad (5.19.27)$$

$$\psi_4(E_1) = \frac{1}{2}[\phi_2 + \phi_3 - \phi_5 - \phi_6] \quad (5.19.28)$$

$$\psi_5(E_2) = \frac{1}{\sqrt{12}}[2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6] \quad (5.19.29)$$

$$\psi_6(E_2) = \frac{1}{2}[\phi_2 - \phi_3 + \phi_5 - \phi_6] \quad (5.19.30)$$

From the characters of the operations  $C_6$ ,  $C_6^2$  ( $= C_3$ ),  $C_6^3$  ( $= C_2$ ),  $C_6^4$  ( $= C_3^2$ ) and  $C_6^5$  associated with the group  $D_{6h}$  (to which benzene belongs), it is obvious that the representations  $A_g$ ,  $B_g$ ,  $E_{1g}$  and  $E_{2g}$  correspond to  $A_{2u}$ ,  $B_{2u}$ ,  $E_{1u}$  and  $E_{2u}$ , respectively.

## 20 FORMATION OF HYBRID ORBITALS

HYBRIDIZATION INVOLVING  $\sigma$ -ORBITALS

The hybrid orbitals of an atom is obtained by mixing atomic orbitals of the same atom. The bonding in a molecule  $AB_n$  may be described in terms of hybrid orbitals of the central atom A. The constituent atomic orbitals in a hybrid orbital can be predicted from the reducible representation of the molecule of which bond vectors form its basis. The following example illustrates the procedure.

sample of Planar  $3_2$ 

The planar  $AB_3$  molecule (assume to lie in the  $xy$  plane) belongs to the point group  $D_{3h}$ . The bond vectors coincide with the three hybrid orbitals of the atom A. These orbitals point towards the atoms B with each bond angle equal to  $120^\circ$ . The character of reducible representation based on bond vectors may be worked out by following the guideline stated as follows.

*The character of reducible representation of a symmetry operation is equal to the number of unshifted bond vectors.*

The set of characters for the symmetry operations of the point group  $D_{3h}$  is shown in Table 5.20.1.

**Table 5.20.1 Reducible Representation based on Bond Vectors of  $AB_3$  Molecule belonging to the Point Group  $D_{3h}$**

Operation	Number of unshifted vectors	Character
$E$	Each of the three bond vectors remains unshifted	3
$2C_3$	All the three bond vectors are shifted	0
$3C_2$	One bond vector coinciding with rotation axis remains unshifted	1
$\sigma_h$	All the three bond vectors remain unshifted	3
$2S_3$	All the three bond vectors are shifted	0
$3\sigma_v$	One bond vector lying in the symmetry plane remains unshifted	1

The resolution of reducible representation in terms of irreducible representations of the point group  $D_{3h}$  can be carried by using the expression

$$a_i = \frac{1}{h_i} \sum_C n_C \chi(C) \chi_i(C)$$

For the molecule  $AB_3$ , we have

$$a(A_1') = \frac{1}{12} [1(3)(1) + 2(0)(1) + 3(1)(1) + 1(3)(1) + 2(0)(1) + 3(1)(1)] = 1$$

$$a(A_2') = \frac{1}{12} [1(3)(1) + 2(0)(1) + 3(1)(-1) + 1(3)(1) + 2(0)(1) + 3(1)(-1)] = 0$$

$$a(E') = \frac{1}{12} [1(3)(2) + 2(0)(-1) + 3(1)(0) + 1(3)(2) + 2(0)(-1) + 3(1)(0)] = 1$$

Similarly, it can be shown that

$$a(A_1'') = 0; \quad a(A_2'') = 0 \quad \text{and} \quad a(E'') = 0$$

Hence,

$$\Gamma = A_1' + E' \quad (5.20.1)$$

From the character table of the point group  $D_{3h}$ , we find that the atomic orbitals which form the bases of  $A_1'$  and  $E'$  are as follows

$$A_1' \quad s \quad (5.20.2)$$

$$E' \quad (p_x, p_y) \quad \text{or/and} \quad (d_{x^2-y^2}, d_{xy}) \quad (5.20.3)$$

Hence, the hybrid orbitals of the central atom A involve either  $s + p_x + p_y$  (i.e.  $sp^2$  hybridization) or  $s + d_{x^2-y^2} + d_{xy}$  (i.e.  $sd^2$  hybridization). However, the scheme  $sd^2$  for molecules  $BH_3$ ,  $BCl_3$  and  $CH_3$  may be excluded since the 3d orbitals have much larger energy as compared to 2s orbital.

The three equivalent  $sp^2$  hybrid orbitals may be represented as follows.

$$\psi_{sp^2_1} = C_{11} \psi_{2s} + C_{12} \psi_{2p_x} + C_{13} \psi_{2p_y} \quad (5.20.4)$$

$$\psi_{sp^2_2} = C_{21} \psi_{2s} + C_{22} \psi_{2p_x} + C_{23} \psi_{2p_y} \quad (5.20.5)$$

$$\psi_{sp^2_3} = C_{31} \psi_{2s} + C_{32} \psi_{2p_x} + C_{33} \psi_{2p_y} \quad (5.20.6)$$

In the matrix notations, we have

$$\begin{bmatrix} \psi_{sp^2_1} \\ \psi_{sp^2_2} \\ \psi_{sp^2_3} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{bmatrix} \begin{bmatrix} \psi_{2s} \\ \psi_{2p_x} \\ \psi_{2p_y} \end{bmatrix} \quad (5.20.7)$$

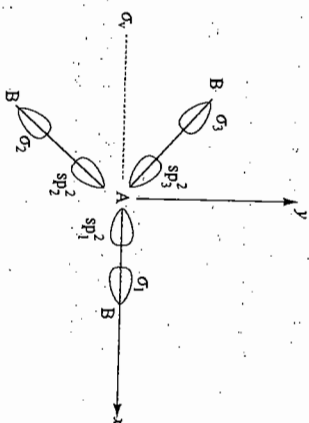
From this, it follows that

$$\begin{bmatrix} \psi_{2s} \\ \psi_{2p_x} \\ \psi_{2p_y} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{bmatrix}^{-1} \begin{bmatrix} \psi_{sp^2_1} \\ \psi_{sp^2_2} \\ \psi_{sp^2_3} \end{bmatrix} \quad (5.20.8)$$

The inverse of matrix C can be obtained by transposing the matrix if the latter represents an orthogonal matrix.

The projection operator technique is used to transform a set of equivalent orbitals (these may be identified with the hybrid orbitals of the central atom A or with the  $\sigma$  orbitals of the pendent atoms B) into symmetry-adapted linear combinations (see Fig. 5.20.1). The obtained set of coefficients in SALC's may be identified with the matrix  $C^{-1}$ . The inverse of this matrix (which is C) is obtained by taking its transpose, which on substitution in Eq. (5.20.7) gives the expressions of set of hybrid orbitals on the central atom A.

Fig. 5.20.1 The equivalent orbitals of atom A and atoms B



For the planar  $AB_3$  molecule, the SALC's obtained by using the equivalent atomic orbitals of atoms B are as follows:

$$\psi_1^{(A)} = \frac{1}{\sqrt{3}} [\sigma_1^A + \sigma_2^A + \sigma_3^A] \quad (\text{Eq. 5.18.16})$$

$$\psi_2^{(E)} = \frac{1}{\sqrt{6}} [2\sigma_1^A - \sigma_2^A - \sigma_3^A] \quad (\text{Eq. 5.18.17})$$

$$\psi_3^{(E)} = \frac{1}{\sqrt{2}} [\sigma_2^A - \sigma_3^A] \quad (\text{Eq. 5.18.18})$$

In terms of hybrid orbitals centred on atom A, we will get

$$\psi_1^{(A)} = \frac{1}{\sqrt{3}} [\psi_{sp^2}^A + \psi_{sp^2}^A + \psi_{sp^2}^A] \quad (5.20.7)$$

$$\psi_2^{(E)} = \frac{1}{\sqrt{6}} [2\psi_{sp^2}^A - \psi_{sp^2}^A - \psi_{sp^2}^A] \quad (5.20.8)$$

$$\psi_3^{(E)} = \frac{1}{\sqrt{2}} [\psi_{sp^2}^A - \psi_{sp^2}^A] \quad (5.20.9)$$

The SALC  $\psi_1$  may be identified with  $\psi_{2s(A)}$  as both belong to the  $A_1'$  representation.

The SALC  $\psi_2$  may be identified with  $\psi_{2p_x(A)}$  as both remain unchanged on applying the operator  $\hat{\sigma}_v$ .

The SALC  $\psi_3$  may be identified with  $\psi_{2p_z(A)}$  as both change sign on applying the operator  $\hat{\sigma}_v$ .

Hence, we write

$$\psi_{2s(A)} = \frac{1}{\sqrt{3}} [\psi_{sp^2}^A + \psi_{sp^2}^A + \psi_{sp^2}^A] \quad (5.20.10)$$

$$\psi_{2p_x(A)} = \frac{1}{\sqrt{6}} [2\psi_{sp^2}^A - \psi_{sp^2}^A - \psi_{sp^2}^A] \quad (5.20.11)$$

$$\psi_{2p_z(A)} = \frac{1}{\sqrt{2}} [\psi_{sp^2}^A - \psi_{sp^2}^A] \quad (5.20.12)$$

In the matrix notation, we write

$$\begin{bmatrix} \psi_{2s} \\ \psi_{2p_x} \\ \psi_{2p_z} \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} \psi_{sp^2}^A \\ \psi_{sp^2}^A \\ \psi_{sp^2}^A \end{bmatrix}$$

From this, we get

$$\begin{bmatrix} \psi_{sp^2}^A \\ \psi_{sp^2}^A \\ \psi_{sp^2}^A \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix}^{-1} \begin{bmatrix} \psi_{2s} \\ \psi_{2p_x} \\ \psi_{2p_z} \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} \psi_{2s} \\ \psi_{2p_x} \\ \psi_{2p_z} \end{bmatrix}$$

$$\text{that is } \psi_{sp^2}^A = \frac{1}{\sqrt{3}} \psi_{2s} + \frac{2}{\sqrt{6}} \psi_{2p_x} \quad (5.20.13)$$

$$\psi_{sp^2}^A = \frac{1}{\sqrt{3}} \psi_{2s} - \frac{1}{\sqrt{6}} \psi_{2p_x} + \frac{1}{\sqrt{2}} \psi_{2p_z} \quad (5.20.14)$$

$$\psi_{sp^2}^A = \frac{1}{\sqrt{3}} \psi_{2s} - \frac{1}{\sqrt{6}} \psi_{2p_x} - \frac{1}{\sqrt{2}} \psi_{2p_z} \quad (5.20.15)$$

The structure of methane can be drawn within a cube as shown in Fig. 5.20.2. It is a tetrahedral molecule and belongs to the point group  $T_d$ . The bond vectors coincide with the four hybrid orbitals of carbon and point towards hydrogen atoms. The set of characters of the reducible representation based on these vectors is shown in Table 5.20.2.

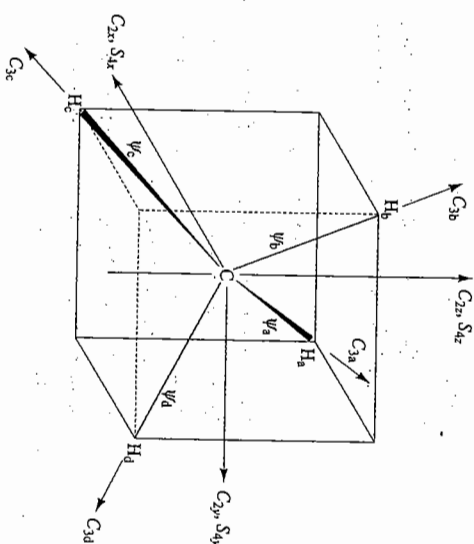


Fig. 5.20.2 Methane molecule

Table 5.20.3 Transformation of Hybrid Orbitals of Carbon under the Symmetry Operations of the Point Group  $T_d$

$E$	$C_{3a}$	$C_{3b}$	$C_{3c}$	$C_{3d}$	$C_{2x}$	$C_{2y}$	$C_{2z}$
$\psi_a$	$\psi_a$	$\psi_c$	$\psi_d$	$\psi_b$	$\psi_c$	$\psi_d$	$\psi_b$
$\psi_b$	$\psi_b$	$\psi_d$	$\psi_a$	$\psi_c$	$\psi_d$	$\psi_b$	$\psi_c$
$\psi_c$	$\psi_c$	$\psi_a$	$\psi_b$	$\psi_d$	$\psi_b$	$\psi_c$	$\psi_d$
$\psi_d$	$\psi_d$	$\psi_b$	$\psi_c$	$\psi_a$	$\psi_c$	$\psi_d$	$\psi_b$
$S_{4x}$	$S_{4y}$	$S_{4z}$	$S_{4c}$	$S_{4d}$	$S_{4e}$	$S_{4f}$	$S_{4g}$
$\psi_a$	$\psi_b$	$\psi_c$	$\psi_d$	$\psi_a$	$\psi_b$	$\psi_c$	$\psi_d$
$\psi_b$	$\psi_c$	$\psi_d$	$\psi_a$	$\psi_b$	$\psi_c$	$\psi_d$	$\psi_a$
$\psi_c$	$\psi_d$	$\psi_a$	$\psi_b$	$\psi_c$	$\psi_d$	$\psi_a$	$\psi_b$
$\psi_d$	$\psi_a$	$\psi_b$	$\psi_c$	$\psi_d$	$\psi_a$	$\psi_b$	$\psi_c$

The four SALC's involving hybrid orbitals of carbon are as follows.

- The application of  $\hat{P}_{A_1}$  on  $\psi_a$  results into  
 $A_1$  symmetry  $\psi'_1 = 6\psi_a + 6\psi_b + 6\psi_c + 6\psi_d$
- The application of  $\hat{P}_{T_2}$  on  $\psi_a$  results into  
 $T_2$  symmetry  $\psi'_2 = 6\psi_a - 2\psi_b - 2\psi_c - 2\psi_d$
- The application of  $\hat{P}_{T_2}$  on  $\psi_b$  results into  
 $T_2$  symmetry  $\psi'_3 = -2\psi_a + 6\psi_b - 2\psi_c - 2\psi_d$
- The application of  $\hat{P}_{T_2}$  on  $\psi_c$  results into  
 $T_2$  symmetry  $\psi'_4 = -2\psi_a - 2\psi_b + 6\psi_c - 2\psi_d$

The wavefunction  $\psi'_1$  is orthogonal to  $\psi'_2$ ,  $\psi'_3$  and  $\psi'_4$ . But the functions  $\psi'_2$ ,  $\psi'_3$  and  $\psi'_4$  are not orthogonal to each other. However, the orthogonal set can be constructed as follows.

$$\begin{aligned}
 A_1 \text{ representation} \quad \psi'_1 &= \psi'_1 = 6\psi_a + 6\psi_b + 6\psi_c + 6\psi_d \\
 T_2 \text{ representation} \quad \psi'_2 &= \psi'_2 = 4\psi_a + 4\psi_b - 4\psi_c - 4\psi_d \\
 \psi'_3 &= \psi'_3 = 4\psi_a - 4\psi_b + 4\psi_c - 4\psi_d \\
 \psi'_4 &= \psi'_4 = 4\psi_a - 4\psi_b - 4\psi_c + 4\psi_d
 \end{aligned}$$

The orthonormal set of these hybrid orbitals are as follows.

$$\begin{aligned}
 A_1 \text{ representation} \quad \psi_1 &= \frac{1}{2}(\psi_a + \psi_b + \psi_c + \psi_d) \\
 T_2 \text{ representation} \quad \psi_2 &= \frac{1}{2}(\psi_a + \psi_b - \psi_c - \psi_d) \\
 \psi_3 &= \frac{1}{2}(\psi_a - \psi_b + \psi_c - \psi_d) \\
 \psi_4 &= \frac{1}{2}(\psi_a - \psi_b - \psi_c + \psi_d)
 \end{aligned}$$

Table 5.20.2 Reducible Representation based on the Bond Vectors of  $CH_4$  Molecule

Operation	Number of unshifted vectors	Character
$E$	Each of the four bonds remains unshifted	4
$8C_3$	Bond vector coinciding with the rotational axis remains unshifted	1
$3C_2$	All the four bonds are shifted	0
$6S_4$	All the four bonds are shifted	0
$6\sigma_d$	Two vectors lying in the reflection plane remain unshifted	2

The irreducible representations contained in the reducible representation are as follows.

$$\begin{aligned}
 a(A_1) &= \frac{1}{24} [1(4)(1) + 8(1)(1) + 3(0)(1) + 6(0)(1) + 6(2)(1)] = 1 \\
 a(A_2) &= \frac{1}{24} [1(4)(1) + 8(1)(1) + 3(0)(1) + 6(0)(-1) + 6(2)(-1)] = 0 \\
 a(E) &= \frac{1}{24} [1(4)(2) + 8(1)(-1) + 3(0)(2) + 6(0)(0) + 6(2)(0)] = 0 \\
 a(T_1) &= \frac{1}{24} [1(4)(3) + 8(1)(0) + 3(0)(-1) + 6(0)(+1) + 6(2)(-1)] = 0 \\
 a(T_2) &= \frac{1}{24} [1(4)(3) + 8(1)(0) + 3(0)(-1) + 6(0)(-1) + 6(2)(1)] = 1
 \end{aligned}$$

Hence,  $\Gamma_{\text{bond vector}} = A_1 + T_2$

From the character table of the point group  $T_d$ , we find that the atomic orbitals which form the bases of  $A_1$  and  $T_2$  representations are as follows.

$$\begin{aligned}
 A_1 \quad s \\
 T_2 \quad (p_x, p_y, p_z) \quad \text{or/and} \quad (d_{xy}, d_{xz}, d_{yz})
 \end{aligned}$$

Hence, the hybrid orbitals of carbon atom involves either  $s + p_x + p_y + p_z$  (i.e.  $sp^3$  hybridization) or  $s + d_{xy} + d_{xz} + d_{yz}$  (i.e.  $sd^3$  hybridization). However, the scheme  $sd^3$  may be excluded since the 3d orbitals of carbon have much larger energy as compared to its 2s orbitals.

Table 5.20.3 includes the results of applying the symmetry operations of the point group  $T_d$  to the hybrid orbitals (represented as  $\psi_a$ ,  $\psi_b$ ,  $\psi_c$  and  $\psi_d$ ) of carbon atom.

The wavefunction  $\psi_1$  may be identified with  $\psi_{2s(C)}$  as bond belong to the  $A_1$  representation.

The wavefunction  $\psi_2$  may be identified with  $\psi_{2p_z(C)}$  as  $\psi_a$  and  $\psi_b$  have positive components along the +z axis and  $\psi_c$  and  $\psi_d$  have negative components along the +z axis.

The wavefunction  $\psi_3$  may be identified with  $\psi_{2p_x(C)}$  as  $\psi_a$  and  $\psi_c$  have positive components along the +x axis and  $\psi_b$  and  $\psi_d$  have negative components along the +x axis.

The wavefunction  $\psi_4$  may be identified with  $\psi_{2p_y(C)}$  as  $\psi_a$  and  $\psi_d$  have positive components along the +y axis and  $\psi_b$  and  $\psi_c$  have negative components along the +y axis.

Hence, we can write

$$\begin{bmatrix} \psi_{2s} \\ \psi_{2p_x} \\ \psi_{2p_y} \\ \psi_{2p_z} \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 & 1 \\ 2 & 2 & 2 & 2 \\ 1 & -1 & 1 & -1 \\ 2 & -2 & 1 & -2 \end{bmatrix} \begin{bmatrix} \psi_a \\ \psi_b \\ \psi_c \\ \psi_d \end{bmatrix}$$

Thus

$$\begin{bmatrix} \psi_a \\ \psi_b \\ \psi_c \\ \psi_d \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 & 1 \\ 2 & 2 & 2 & 2 \\ 1 & -1 & 1 & -1 \\ 2 & -2 & 1 & -2 \end{bmatrix}^{-1} \begin{bmatrix} \psi_{2s} \\ \psi_{2p_x} \\ \psi_{2p_y} \\ \psi_{2p_z} \end{bmatrix}$$

This gives

$$\psi_{sp^3_1} = \frac{1}{2} (\psi_{2s} + \psi_{2p_x} + \psi_{2p_y} + \psi_{2p_z})$$

$$\psi_{sp^3_2} = \frac{1}{2} (\psi_{2s} - \psi_{2p_x} - \psi_{2p_y} + \psi_{2p_z})$$

$$\psi_{sp^3_3} = \frac{1}{2} (\psi_{2s} + \psi_{2p_x} - \psi_{2p_y} - \psi_{2p_z})$$

$$\psi_{sp^3_4} = \frac{1}{2} (\psi_{2s} - \psi_{2p_x} + \psi_{2p_y} - \psi_{2p_z})$$

### EXAMPLE OF $AB_3$ MOLECULE

#### HYBRIDIZATION INVOLVING $\pi$ -ORBITALS

A  $\pi$ -orbital is defined as one which has one nodal plane containing the bond axis. For each B atom in the planar  $AB_3$ , there are two 2p orbitals (namely,  $2p_x$  and  $2p_y$ ) of  $\pi$ -nature. Of these, one is in the molecular plane perpendicular to A—B bond and the second one is perpendicular to the molecular plane (Fig. 5.20.3). These may be represented by vectors pointing in the appropriate directions and are referred to as  $\pi(I)$  and  $\pi(L)$  orbitals respectively.

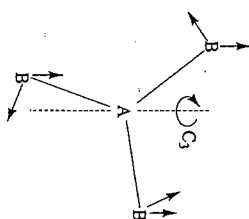


Fig. 5.20.3 Vectors representing  $\pi$ -orbitals of B atoms in the planar  $AB_3$  molecule

The two sets of  $\pi$ -orbitals may be treated separately as no vector of one set is interchanged with the vector of the second set under the symmetry operations of the group  $D_{3h}$ . Thus, each of the two sets may be considered separately as a basis for a reducible representation.

The character of a symmetry operation may be determined based on the following facts.

- (i) A displaced vector contributes zero.
- (ii) An undisplaced vector without changing direction contributes +1.
- (iii) An undisplaced vector with changing direction in the opposite contributes -1.

The following are the characters of reducible representations based on all the six  $\pi$ -orbitals and those based on the two sets of  $\pi$ -orbitals.

	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3C_2'$
$\Gamma_\pi$	6	0	-2	0	0	0
$\Gamma_{\pi(I)}$	3	0	-1	3	0	-1
$\Gamma_{\pi(L)}$	3	0	-1	-3	0	1

The resolution of two reducible representations in terms of irreducible representations of the point group  $D_{3h}$  are as follows.

$$\begin{aligned} \Gamma_{\pi(I)} &= A_2' + E' \\ \Gamma_{\pi(L)} &= A_2'' + E'' \end{aligned}$$

The orbitals belonging to the above irreducible representations (see character table) are as follows.

$$\begin{aligned} A_2' : & \text{none} \\ E' : & (p_x, p_y) \text{ and } (d_{x^2-y^2}, d_{xy}) \\ A_2'' : & p_z \\ E'' : & (d_{xz}, d_{yz}) \end{aligned}$$

### Formation of $\pi$ -Orbitals

#### Irreducible Representations



From these, the following conclusions can be drawn.

- The orbitals  $\pi(\perp)$  can form bonds with atom A involving  $pd^2$  hybridization which includes  $p_z$ ,  $d_{xz}$  and  $d_{yz}$  orbitals.
- The orbitals  $\pi(\parallel)$  can form two bonds with atom A involving  $p_x$  and  $p_y$  (or  $d_{x^2-y^2}$  and  $d_{xy}$ ) orbitals. These two bonds are shared equally among the three B atoms.

### EXAMPLE OF $AB_6$ MOLECULE

The molecule  $AB_6$  has octahedral structure (Fig. 5.20.4). The two  $\pi$ -orbitals associated with each B atom are also shown in Fig. 5.20.4.

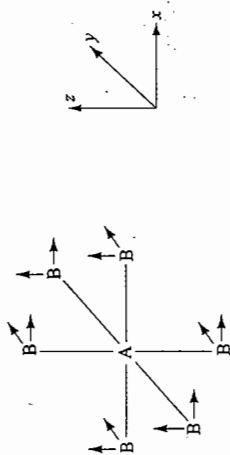


Fig. 5.20.4 Twelve  $\pi$ -orbitals of the B atoms in  $AB_6$  molecule

### Reducible Representations

Each vector is exchanged with each of the other eleven by one symmetry operation or another of the point group  $O_h$ . This implies that all the twelve orbitals of atoms B (and also those of atom A) have to be considered together as a basis of reducible representation. The characters of symmetry operations of the reducible representation are as follows.

$O_h$	$E$	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	$i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma_\pi$	12	0	0	0	-4	0	0	0	0	0

From the character table of  $O_h$  group, it can be verified that

$$\Gamma_\pi = \Gamma_{1g} + \Gamma_{2g} + \Gamma_{1u} + \Gamma_{2u}$$

Also the orbitals belonging to above irreducible representations are as follows.

$$\Gamma_{1g} : \text{none}$$

$$\Gamma_{2g} : (d_{xy}, d_{xz}, d_{yz})$$

$$\Gamma_{1u} : (p_x, p_y, p_z)$$

$$\Gamma_{2u} : \text{none}$$

### Formation of $\pi$ -Orbitals

The following conclusion can be drawn for  $\pi$ -bondings in  $AB_6$  molecule.

- Since six atomic orbitals of atom A are used in forming six  $\sigma$  bonds with B atoms, it is not possible to form the entire set of twelve A—B  $\pi$ -bonds.
- The p's orbitals of A must have been used in forming  $\sigma$  bonds with the appropriate orbitals of atoms B. Thus, p orbitals of atom A cannot form any  $\pi$ -bond with B atoms.
- Only the three d orbitals of atom A can be used in the  $\pi$ -bonds formation. It can be said that the three  $\pi$ -bonds shared equally among the six A—B pairs are formed in  $AB_6$  molecule.

### Problem 5.20.1

Form the hybrid orbitals of atom A involved in the  $\sigma$  bondings with the four B atoms in a planar  $AB_4$  molecule. Also analyse the hybridization in  $\pi$ -bondings.

The planar molecule  $AB_4$  (Fig. 5.20.5) belongs to the group  $D_{4h}$ . The reducible representation based on its four bond vectors is as follows.

$\Gamma_{\text{bond}}$	$E$	$2C_4$	$C_2$	$2C_2'$	$2C_2''$	$i$	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$
	4	0	0	2	0	0	0	4	2	0

The irreducible representations in the above reducible representation are as follows.

$$\alpha(A_{1g}) = \frac{1}{16} [1(4)(1) + 2(2)(1) + 1(4)(1) + 1(2)(1)] = 1$$

$$\alpha(B_{1g}) = \frac{1}{16} [1(4)(1) + 2(2)(1) + 1(4)(1) + 1(2)(1)] = 1$$

$$\alpha(E_u) = \frac{1}{16} [1(4)(2) + 2(2)(0) + 1(4)(2) + 1(2)(0)] = 1$$

$$\text{Hence } \Gamma_{\text{bond}} = \Gamma_{A_{1g}} + \Gamma_{B_{1g}} + \Gamma_{E_u}$$

From the character table of  $D_{4h}$ , we find that

$$\Gamma_{A_{1g}} : s, d_{z^2}$$

$$\Gamma_{B_{1g}} : d_{x^2-y^2}$$

$$\Gamma_{E_u} : p_x, p_y$$

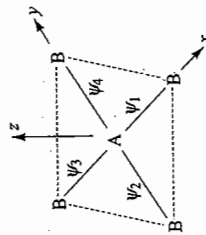


Fig. 5.20.5 The planar  $AB_4$  molecule

### Formation of Hybrid Orbitals

Hence, the atom involves  $dsp^2$  hybridization (or  $d^2p^2$ ). We consider here  $dsp^2$  hybridization. The SALC's involving hybrid orbitals may be determined by using  $C_4$  symmetry.

$$\begin{aligned} \hat{P}_{A_{1g}} \psi_1 &= \chi_{A_{1g}}(E) \{E\psi_1\} + \chi_{A_{1g}}(C_4) \{C_4^3\psi_1\} + \chi_{A_{1g}}(C_2) \{C_2^2\psi_1\} + \chi_{A_{1g}}(C_4) \{C_4\psi_1\} \\ &= (1)\psi_1 + (1)\psi_2 + (1)\psi_3 + (1)\psi_4 \end{aligned}$$

$$\text{The normalized function is } \varphi_1 = \frac{1}{2} (\psi_1 + \psi_2 + \psi_3 + \psi_4)$$

$$\hat{P}_{B_{1g}} \psi_1 = (1)\psi_1 + (-1)\psi_2 + (1)\psi_3 + (-1)\psi_4$$

$$\text{The normalized function is } \varphi_2 = \frac{1}{2} (\psi_1 - \psi_2 + \psi_3 - \psi_4)$$

$$\hat{P}_{E_u} \psi_1 = (2)\psi_1 + (0)\psi_2 + (-2)\psi_3 + (0)\psi_4$$

The normalized function is  $\phi_3 = \frac{1}{\sqrt{2}}(\psi_1 - \psi_3)$

$$\hat{P}_E \psi_2 = (2)\psi_2 + (0)\psi_3 + (-2)\psi_4 + (0)\psi_1$$

The normalized function is  $\phi_4 = \frac{1}{\sqrt{2}}(\psi_2 - \psi_4)$

The identification of  $\phi_1$  to  $\phi_4$  with atomic orbitals is as follows.

$A_{1g}$  representation  $\phi_1 = \psi_{2s}$

$B_{1g}$  representation  $\phi_2 = \psi_{d_{x^2-y^2}}$

$E_u$  representation  $\begin{cases} \phi_3 = \psi_{p_x}; \psi_1 \text{ and } \psi_3 \text{ lie along } x \text{ axis} \\ \phi_4 = \psi_{p_y}; \psi_2 \text{ and } \psi_4 \text{ lie along } y \text{ axis} \end{cases}$

Hence

$$\begin{bmatrix} \psi_{2s} \\ \psi_{d_{x^2-y^2}} \\ \psi_{p_x} \\ \psi_{p_y} \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & 0 & 0 & -\frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix}$$

This gives

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & 0 & 0 & -\frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \end{bmatrix}^{-1} \begin{bmatrix} \psi_{2s} \\ \psi_{d_{x^2-y^2}} \\ \psi_{p_x} \\ \psi_{p_y} \end{bmatrix}$$

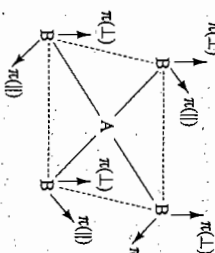
$$= \begin{bmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{bmatrix} \begin{bmatrix} \psi_{2s} \\ \psi_{d_{x^2-y^2}} \\ \psi_{p_x} \\ \psi_{p_y} \end{bmatrix}$$

This gives

$$\begin{aligned} \psi_1 &= \frac{1}{2}\psi_{2s} + \frac{1}{2}\psi_{d_{x^2-y^2}} + \frac{1}{\sqrt{2}}\psi_{p_x} \\ \psi_2 &= \frac{1}{2}\psi_{2s} - \frac{1}{2}\psi_{d_{x^2-y^2}} + \frac{1}{\sqrt{2}}\psi_{p_y} \end{aligned}$$

## Analysis of $\pi$ -Hybridization

Fig. 5.20.6  $\pi$ -orbitals of B atoms in a planar  $AB_4$  molecule



$$\begin{aligned} \psi_3 &= \frac{1}{2}\psi_{2s} + \frac{1}{2}\psi_{d_{x^2-y^2}} - \frac{1}{\sqrt{2}}\psi_{p_x} \\ \psi_4 &= \frac{1}{2}\psi_{2s} - \frac{1}{2}\psi_{d_{x^2-y^2}} - \frac{1}{\sqrt{2}}\psi_{p_y} \end{aligned}$$

Figure 5.20.6 displays the eight  $\pi$ -orbitals of the four B atoms in a planar  $AB_4$  molecule.

The  $\pi(L)$  orbitals are not interchanged with any of  $\pi(H)$  orbital under the symmetry operations of the group  $D_{4h}$ . Hence, these may be treated separately as far as the bases of reducible representations are concerned. Hence, we have

	E	$2C_4$	$C_2$	$2C_2'$	$2C_2''$	$i$	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$
$\Gamma_{\pi(H)}$	4	0	0	-2	0	0	0	4	-2	0
$\Gamma_{\pi(L)}$	4	0	0	-2	0	0	0	-4	2	0

Their resolution in the irreducible representations gives

$$\Gamma_{\pi(H)} = \Gamma_{A_g} + \Gamma_{B_g} + \Gamma_{E_g}$$

$$\Gamma_{\pi(L)} = \Gamma_{A_g} + \Gamma_{B_g} + \Gamma_{E_g}$$

The orbitals involved in these irreducible representations are

$$\begin{array}{lll} A_{2g} : \text{none} & B_{2g} : d_{xy} & E_u : (p_x, p_y) \\ A_{2u} : p_z & B_{2u} : \text{none} & E_g : (d_{xz}, d_{yz}) \end{array}$$

The conclusions regarding  $\pi$ -bonds are as follows.

- Neither of the two sets will form complete bonding as the orbitals (among s, p and d) do not exist under the representation  $A_{2g}$  and  $B_{2u}$ , respectively.
- Among parallel  $\pi$ -orbitals, only  $d_{xy}$  orbital is available since  $p_x$  and  $p_y$  orbitals are already involved in  $\sigma$  bondings. Hence, only one  $\pi$ -bond in molecular plane shared equally among all four A—B pairs is possible.
- Among perpendicular orbitals, only  $p_x$ ,  $d_{xz}$  and  $d_{yz}$  orbitals are available. Hence three  $\pi$ -bonds perpendicular to the molecular plane shared equally among all four A—B pairs are possible.

## 5.21 PREDICTING ZERO VALUE OF AN INTEGRAL

### Introduction

Consider the integrals

$$\int_{-a}^{+a} x dx = \frac{x^2}{2} \Big|_{-a}^{+a} = \frac{a^2}{2} - \frac{(-a)^2}{2} = 0$$

$$\int_{-a}^{+a} x^2 dx = \frac{x^3}{3} \Big|_{-a}^{+a} = \frac{a^3}{3} - \frac{(-a)^3}{3} = \frac{2}{3}a^3$$

In general, if the integrand is odd, i.e.  $f(x) = -f(-x)$ , then the integral of the above type results into a zero value. If the integrand is even, i.e.  $f(x) = f(-x)$ , then the integral results into a nonzero value. The above generalization can be extended to more involved integrals which appear in many applications of quantum chemistry.

In the evaluation of electronic energies in an atom or a molecule, one encounters integrals of the type

$$H_{ij} = \int \psi_i H_{op} \psi_j d\tau \quad (5.21.1)$$

where  $H_{op}$  is Hamiltonian operator and  $\psi_i$  and  $\psi_j$  are the orbitals.

The Hamiltonian operator is an energy operator. Since the latter is no way affected by the symmetry operations, it belongs to the totally symmetric representation. The symmetry of the integrand in the above integral depends on the representations contained in the direct product of the representations of  $\psi_i$  and  $\psi_j$ . This direct product will yield totally symmetric representation only when both  $\psi_i$  and  $\psi_j$  belong to the same irreducible representation. Hence, the criterion of the integral  $H_{ij}$  having a nonzero value is as follows.

Both  $\psi_i$  and  $\psi_j$  must belong to the same irreducible representation of the molecular point group.

## ILLUSTRATION OF trans-BUTADIENE

If we adopt  $2p_z$  orbitals (represented as  $\phi_1, \phi_2, \phi_3$  and  $\phi_4$ ) as the basis of constructing molecular orbitals of *trans*-butadiene (Fig. 5.21.1.), we would write the molecular orbitals as

$$\psi_{MO} = C_1\phi_1 + C_2\phi_2 + C_3\phi_3 + C_4\phi_4 \quad (5.21.2)$$

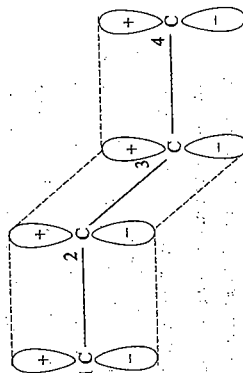


Fig. 5.21.1 *Trans*-Butadiene

The energies of molecular orbitals, under Hückel approximations, are given by the secular determinant,

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad (5.21.3)$$

On opening this determinant, we get an expression of fourth power in  $E$  which can be solved to give the following roots.

$$E = \alpha + 1.618 \beta \quad E' = \alpha + 0.618 \beta$$

$$E'' = \alpha - 0.618 \beta \quad E''' = \alpha - 1.618 \beta \quad (5.21.4)$$

Substituting these energies one by one in secular equations along with the normalization expression of molecular orbital provides the values of coefficients  $C_1, C_2, C_3$  and  $C_4$ .

However, the calculations are simplified if we adopt the following symmetry-adapted linear combinations (Eqs 5.18.70 to 5.18.74),

$$B_g: \quad \psi_1 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_4) \quad \text{and} \quad \psi_2 = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) \quad (5.21.5)$$

$$A_u: \quad \psi_3 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_4) \quad \text{and} \quad \psi_4 = \frac{1}{\sqrt{2}}(\phi_2 + \phi_3) \quad (5.21.6)$$

Knowing the fact that the matrix element  $\langle \psi_i | H_{op} | \psi_j \rangle$  is zero unless  $\psi_i$  and  $\psi_j$  belong to the same irreducible representation, the secular determinant for the molecular orbital

$$\psi_{MO} = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + C_4\psi_4 \quad (5.21.7)$$

takes the following form.

$$\begin{vmatrix} H_{11} - E & H_{12} & 0 & 0 \\ H_{21} & H_{22} - E & 0 & 0 \\ 0 & 0 & H_{33} - E & H_{34} \\ 0 & 0 & H_{43} & H_{44} - E \end{vmatrix} = 0 \quad (5.21.8)$$

This determinant is factored into two determinants:

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0 \quad \text{and} \quad \begin{vmatrix} H_{33} - E & H_{34} \\ H_{43} & H_{44} - E \end{vmatrix} = 0 \quad (5.21.9)$$

Thus, we get all the four energies by solving two determinants of the order  $2 \times 2$  instead of one determinant of the order  $4 \times 4$ . This way, the symmetry of the molecule helps simplifying the molecular calculations.

In the present case, we have

$$\begin{aligned} H_{11} &= \frac{1}{2} \langle (\phi_1 - \phi_4) | H_{op} | (\phi_1 - \phi_4) \rangle \\ &= \frac{1}{2} \{ \langle \phi_1 | H_{op} | \phi_1 \rangle - \langle \phi_1 | H_{op} | \phi_4 \rangle - \langle \phi_4 | H_{op} | \phi_1 \rangle + \langle \phi_4 | H_{op} | \phi_4 \rangle \} \end{aligned}$$

Under the Hückel approximations, this reduces to

$$H_{11} = \frac{1}{2} [\alpha - 0 - 0 + \alpha] = \alpha$$

Similarly, working with other matrix elements of the first determinant, we will get

$$H_{22} = \alpha - \beta$$

$$H_{12} = H_{21} = \beta$$

Hence, the first secular determinant becomes

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & (\alpha - \beta) - E \end{vmatrix} = 0 \quad \text{or} \quad \begin{vmatrix} x & 1 \\ 1 & x - 1 \end{vmatrix} = 0 \quad \text{where} \quad x = (\alpha - E)/\beta$$

This gives  $x(x-1) - 1 = 0$  i.e.  $x^2 - x - 1 = 0$

Its roots are  $x_1 = \frac{1 - \sqrt{1+4}}{2}$  and  $x_2 = \frac{1 + \sqrt{1+4}}{2}$

$$\text{Hence} \quad \frac{\alpha - E_1}{\beta} = \frac{1 - \sqrt{5}}{2} \Rightarrow E_1 = \alpha + 0.618\beta \quad (5.21.10)$$

$$\text{and} \quad \frac{\alpha - E_2}{\beta} = \frac{1 + \sqrt{5}}{2} \Rightarrow E_2 = \alpha - 1.618\beta \quad (5.21.11)$$

Similarly working with the second determinant, we will get

$$E_3 = \alpha + 1.618\beta \quad \text{and} \quad E_4 = \alpha - 0.618\beta \quad (5.21.12)$$

Substitution of these energies one by one in the corresponding secular equations along with the normalization expression of molecular orbitals provides the coefficients  $C_1, C_2, C_3$  and  $C_4$  in Eq. (5.21.7). For example, for  $E_1 = \alpha + 0.618\beta$ , we get

$$C_1(\alpha - E) + C_2\beta + C_3(0) + C_4(0) = 0$$

$$\text{or} \quad C_1[\alpha - (\alpha + 0.618\beta)] + C_2\beta = 0$$

$$\text{or} \quad C_1 = C_2/0.618$$

Substituting this in the expression  $C_1^2 + C_2^2 = 1$ , we get

$$\left(\frac{C_2}{0.618}\right)^2 + C_2^2 = 1 \Rightarrow C_2^2 = 0.276 \Rightarrow C_2 = 0.526$$

$$C_1 = \frac{C_2}{0.618} = \frac{0.526}{0.618} = 0.851$$

Hence

$$E_1 = \alpha + 0.618\beta \quad \psi_{1,MO}^{(B)} = 0.851\psi_1 + 0.526\psi_2$$

$$\begin{aligned} &= 0.851 \left[ \frac{1}{\sqrt{2}}(\phi_1 - \phi_4) \right] + 0.526 \left[ \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) \right] \\ &= 0.602(\phi_1 - \phi_4) + 0.372(\phi_2 - \phi_3) \end{aligned} \quad (5.21.13)$$

Similarly, working with other energies, we will get

$$E_2 = \alpha - 1.618\beta \quad \psi_{2,MO}^{(B)} = 0.372(\phi_1 - \phi_4) - 0.602(\phi_2 - \phi_3) \quad (5.21.14)$$

$$E_3 = \alpha + 1.618\beta \quad \psi_{3,MO}^{(A)} = 0.372(\phi_1 + \phi_4) + 0.602(\phi_2 + \phi_3) \quad (5.21.15)$$

$$E_4 = \alpha - 0.618\beta \quad \psi_{4,MO}^{(A)} = 0.602(\phi_1 + \phi_4) - 0.372(\phi_2 + \phi_3) \quad (5.21.16)$$

## ILLUSTRATION OF NAPHTHALENE

In Section 5.18, we have formulated the molecular orbitals from SALC's of naphthalene (Eqs. 5.18.79 to 5.18.88). In the molecular orbital treatment, the secular determinant of naphthalene will be factored into the following four determinants (see, Eqs 5.18.89 to 5.18.92).

$$\text{B}_{2g} \text{ symmetry:} \quad \begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0 \quad (5.21.17)$$

$$\text{B}_{3g} \text{ symmetry:} \quad \begin{vmatrix} H_{33} - E & H_{34} & H_{35} \\ H_{43} & H_{44} - E & H_{45} \\ H_{53} & H_{54} & H_{55} - E \end{vmatrix} = 0 \quad (5.21.18)$$

$$\text{A}_u \text{ symmetry:} \quad \begin{vmatrix} H_{66} - E & H_{67} \\ H_{76} & H_{77} - E \end{vmatrix} = 0 \quad (5.21.19)$$

$$\text{B}_{1u} \text{ symmetry:} \quad \begin{vmatrix} H_{88} - E & H_{89} & H_{8,10} \\ H_{98} & H_{99} - E & H_{9,10} \\ H_{10,8} & H_{10,9} & H_{10,10} - E \end{vmatrix} = 0 \quad (5.21.20)$$

## Working for Molecular Orbitals $\psi_1$ and $\psi_2$

Here, we work out the molecular orbitals  $\psi_1$  and  $\psi_2$ . The remaining molecular orbitals can be worked out following the same procedure. We follow Hückel approximations while examining the elements of secular determinants. These are

$$\langle \phi_i | H_{op} | \phi_i \rangle = \alpha$$

$$\text{and} \quad \langle \phi_i | H_{op} | \phi_j \rangle = \beta \quad \text{if } i \text{ and } j \text{ are neighbouring atoms}$$

$$\text{We have} \quad = 0 \quad \text{if } i \text{ and } j \text{ are nonneighbouring atoms}$$

$$\begin{aligned} H_{11} &= \langle \psi_1 | H_{op} | \psi_1 \rangle = \frac{1}{4} \langle (\phi_1 - \phi_5 - \phi_8 + \phi_4) | H_{op} | (\phi_1 - \phi_5 - \phi_8 + \phi_4) \rangle \\ &= \frac{1}{4} [\langle \phi_1 | H_{op} | \phi_1 \rangle + \langle \phi_5 | H_{op} | \phi_5 \rangle + \langle \phi_8 | H_{op} | \phi_8 \rangle + \langle \phi_4 | H_{op} | \phi_4 \rangle] \\ &= \alpha \end{aligned}$$

$$\begin{aligned} H_{12} &= \langle \psi_1 | H_{op} | \psi_2 \rangle = \frac{1}{4} \langle (\phi_1 - \phi_5 - \phi_8 + \phi_4) | H_{op} | (\phi_2 - \phi_6 - \phi_7 + \phi_3) \rangle \\ &= \frac{1}{4} [\langle \phi_1 | H_{op} | \phi_2 \rangle + \langle \phi_5 | H_{op} | \phi_6 \rangle + \langle \phi_8 | H_{op} | \phi_7 \rangle + \langle \phi_4 | H_{op} | \phi_3 \rangle] \\ &= \beta \end{aligned}$$

$$H_{21} = H_{12}$$

$$\begin{aligned}
 H_{22} &= \langle \psi_1 | H_{op} | \psi_2 \rangle = \frac{1}{4} (\langle \psi_2 - \phi_6 - \phi_7 + \phi_3 | H_{op} | \langle \psi_2 - \phi_6 - \phi_7 + \phi_3 \rangle) \\
 &= \frac{1}{4} [\langle \phi_2 | H_{op} | \phi_2 \rangle + \langle \phi_2 | H_{op} | \phi_3 \rangle + \langle \phi_6 | H_{op} | \phi_6 \rangle + \langle \phi_6 | H_{op} | \phi_7 \rangle \\
 &\quad + \langle \phi_7 | H_{op} | \phi_6 \rangle + \langle \phi_7 | H_{op} | \phi_7 \rangle + \langle \phi_3 | H_{op} | \phi_2 \rangle + \langle \phi_3 | H_{op} | \phi_3 \rangle] \\
 &= \alpha + \beta
 \end{aligned}$$

With these, the secular determinant as given by Eq. (5.21.17) becomes

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha + \beta - E \end{vmatrix} = 0 \quad \text{or} \quad \begin{vmatrix} x & 1 \\ 1 & x + 1 \end{vmatrix} = 0 \quad [\text{where } x = (\alpha - E)/\beta]$$

Opening the determinant, we get

$$x(x+1) - 1 = 0 \quad \text{or} \quad x^2 + x - 1 = 0$$

Its roots are

$$x_1 = \frac{-1 - \sqrt{1+4}}{2} = -1.618 \quad \text{and} \quad x_2 = \frac{-1 + \sqrt{1+4}}{2} = 0.618$$

$$\text{Hence} \quad \frac{\alpha - E_1}{\beta} = -1.618 \Rightarrow E_1 = \alpha + 1.618\beta$$

$$\frac{\alpha - E_2}{\beta} = 0.618 \Rightarrow E_2 = \alpha - 0.618\beta$$

The secular equations are

$$C_1(H_{11} - E) + C_2 H_{12} = 0 \quad \text{i.e.} \quad C_1(\alpha - E) + C_2 \beta = 0$$

$$C_1 H_{21} + C_2 (H_{22} - E) = 0 \quad \text{i.e.} \quad C_1 \beta + C_2(\alpha + \beta - E) = 0$$

• For  $E_1 = \alpha + 1.618\beta$ , we get

$$C_1(-1.618\beta) + C_2 \beta = 0 \quad \text{i.e.} \quad C_1/C_2 = 1/1.618 = 0.618$$

From the normalization of  $\psi_1$ , we get

$$C_1^2 + C_2^2 = 1 \Rightarrow (0.618 C_2)^2 + C_2^2 = 1$$

$$\Rightarrow C_2 = \sqrt{1/(1 + 0.618^2)} = 0.850$$

$$\text{Hence } C_1 = (0.618)C_2 = (0.618)(0.850) = 0.526$$

$$\begin{aligned}
 \text{Thus } \psi_1 &= C_1 \psi_1' + C_2 \psi_2' = 0.526 \psi_1' + 0.850 \psi_2' \\
 &= 0.526 \left[ \frac{1}{2} (\phi_1 - \phi_5 - \phi_8 + \phi_4) \right] + 0.850 \left[ \frac{1}{2} (\phi_2 - \phi_6 - \phi_7 + \phi_3) \right] \\
 &= 0.263 (\phi_1 - \phi_5 - \phi_8 + \phi_4) + 0.425 (\phi_2 - \phi_6 - \phi_7 + \phi_3)
 \end{aligned}$$

• For  $E_2 = \alpha - 0.618\beta$ , we get

$$C_1(0.618\beta) + C_2 = 0 \quad \text{i.e.} \quad C_1/C_2 = -1/0.618 = -1.618$$

From the normalization of  $\psi_2$ , we get

$$C_1^2 + C_2^2 = 1 \Rightarrow (-1.618 C_2)^2 + C_2^2 = 1$$

$$\Rightarrow C_2 = \sqrt{1/(1 + 1.618^2)} = 0.526$$

$$\text{Hence } C_1 = (-1.618)C_2 = (-1.618)(0.526) = -0.850$$

## Energies of Remaining MOs

$$\begin{aligned}
 \text{Thus } \psi_2 &= C_1 \psi_1' + C_2 \psi_2' = -0.850 \psi_1' + 0.526 \psi_2' \\
 &= -0.850 \left[ \frac{1}{2} (\phi_1 - \phi_5 - \phi_8 + \phi_4) \right] + 0.526 \left[ \frac{1}{2} (\phi_2 - \phi_6 - \phi_7 + \phi_3) \right] \\
 &= -0.425 (\phi_1 - \phi_5 - \phi_8 + \phi_4) + 0.263 (\phi_2 - \phi_6 - \phi_7 + \phi_3)
 \end{aligned}$$

Working similarly, it can be shown that the energies and wavefunctions of the remaining symmetries are as follows.

### $B_{3g}$ Symmetry

$$E_3 = \alpha + 1.303\beta$$

$$\psi_3 = 0.400 (\phi_1 - \phi_4 - \phi_5 + \phi_8) + 0.174 (\phi_2 - \phi_3 - \phi_6 + \phi_7) + 0.347 (\phi_9 - \phi_{10})$$

$$E_4 = \alpha - \beta$$

$$\psi_4 = 0.408 (\phi_2 - \phi_3 - \phi_6 + \phi_7) - 0.408 (\phi_9 - \phi_{10})$$

$$E_5 = \alpha - 2.303\beta$$

$$\psi_5 = 0.301 (\phi_1 - \phi_4 - \phi_5 + \phi_8) - 0.231 (\phi_2 - \phi_3 - \phi_6 + \phi_7) - 0.461 (\phi_9 - \phi_{10})$$

### $A_u$ Symmetry

$$E_6 = \alpha + 0.168\beta$$

$$\psi_6 = 0.425 (\phi_1 - \phi_4 + \phi_5 - \phi_8) + 0.263 (\phi_2 - \phi_3 + \phi_6 - \phi_7)$$

$$E_7 = \alpha - 1.618\beta$$

$$\psi_7 = 0.263 (\phi_1 - \phi_4 + \phi_5 - \phi_8) - 0.425 (\phi_2 - \phi_3 + \phi_6 - \phi_7)$$

### $B_{1u}$ Symmetry

$$E_8 = \alpha + 2.303\beta$$

$$\psi_8 = 0.301 (\phi_1 + \phi_4 + \phi_5 + \phi_8) + 0.231 (\phi_2 + \phi_3 + \phi_6 + \phi_7) + 0.461 (\phi_9 + \phi_{10})$$

$$E_9 = \alpha + \beta$$

$$\psi_9 = 0.408 (\phi_2 + \phi_3 + \phi_6 + \phi_7) - 0.408 (\phi_9 + \phi_{10})$$

$$E_{10} = \alpha - 1.303\beta$$

$$\psi_{10} = 0.400 (\phi_1 + \phi_4 + \phi_5 + \phi_8) - 0.174 (\phi_2 + \phi_3 + \phi_6 + \phi_7) - 0.347 (\phi_9 + \phi_{10})$$

Work out the Hückel  $\pi$ -molecular orbitals along with their energies for the molecule tetramethylenecyclobutane (assume it to be planar).

The molecule tetramethylenecyclobutane belongs to the point group  $D_{4h}$ . The numbering of atoms is shown in Fig. 5.21.2.

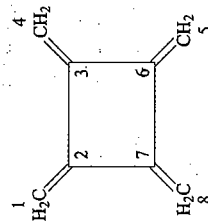


Fig. 5.21.2 A molecule of tetramethylenecyclobutane

## Problem 5.21.1

### Solution

**Two Sets of  $2p_z$  Orbitals**

Each of the eight carbon atoms contributes one  $2p_z$  orbital towards  $\pi$ -molecular orbitals. These orbitals may be divided into two sets since the orbitals in one set ( $2p_z$  orbitals of carbon atoms 1, 4, 5 and 8) are not interchanged with any of the orbitals in the second set ( $2p_z$  orbitals of carbon atoms 2, 3, 6 and 7) under the symmetry operations of the point group  $D_{4h}$ . The two sets may be treated separately to work out SALC's.

Based on the two sets of  $2p_z$  orbitals the reducible representations are as follows.

$D_{4h}$	$E$	$2C_4$	$C_2$	$2C_2'$	$2C_2''$	$i$	$2\sigma_h$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$
$\Gamma_{\text{set 1}}$	4	0	0	0	-2	0	0	-4	0	2
$\Gamma_{\text{set 2}}$	4	0	0	0	-2	0	0	-4	0	2

Both representations being identical will contain the same type and numbers of irreducible representations. Based on the expression

$$a_i = \frac{1}{h} \sum_C n_C \chi(C) \chi_i(C)$$

we get the following representations.

$$a(A_{2u}) = \frac{1}{16} [1(4)(1) + 2(-2)(-1) + 1(-4)(-1) + 2(2)(1)] = 1$$

$$a(B_{1u}) = \frac{1}{16} [1(4)(1) + 2(-2)(-1) + 1(-4)(-1) + 2(2)(1)] = 1$$

$$a(E_g) = \frac{1}{16} [1(4)(2) + 2(-2)(0) + 1(-4)(-2) + 2(2)(0)] = 1$$

Hence  $\Gamma_{\text{set 1}} = A_{2u} + B_{1u} + E_g$  and  $\Gamma_{\text{set 2}} = A_{2u} + B_{1u} + E_g$

These may be generated by considering the symmetries of the group  $C_4$ . We ignore multiplication factors as these are ascertained by the normalization of SALC's.

 **$A_{2u}$  Symmetry**

$$\begin{aligned} \hat{P}_A \phi_1 &= \chi(E) \hat{E} \phi_1 + \chi(C_4) \hat{C}_4 \phi_1 + \chi(C_2) \hat{C}_2 \phi_1 + \chi(C_4^3) \hat{C}_4^3 \phi_1 \\ &= (1)\phi_1 + (1)\phi_4 + (1)\phi_5 + (1)\phi_8 \end{aligned}$$

The normalized SALC is  $\psi_1 = \frac{1}{2}(\phi_1 + \phi_4 + \phi_5 + \phi_8)$

The operation of  $\hat{P}_A$  on  $\phi_2$  (orbital of second set) would give

$$\psi_2 = \frac{1}{2}(\phi_2 + \phi_3 + \phi_6 + \phi_7)$$

 **$B_{1u}$  Symmetry**

$$\hat{P}_B \phi_1 = (1)\phi_1 + (-1)\phi_4 + (1)\phi_5 + (-1)\phi_8$$

The normalized SALC is  $\psi_3 = \frac{1}{2}(\phi_1 - \phi_4 + \phi_5 - \phi_8)$

For the set 2, we have

$$\psi_4 = \frac{1}{2}(\phi_2 - \phi_3 + \phi_6 - \phi_7)$$

 **$E_g$  Symmetry**

$$\hat{P}_E \phi_1 = (1)\phi_1 + (1)\phi_4 + (-1)\phi_5 + (-1)\phi_8$$

i.e.  $\psi_5 = \phi_1 + i\phi_4 - \phi_5 - i\phi_8$

$$\hat{P}_E \phi_1 = (1)\phi_1 + (-i)\phi_4 + (-1)\phi_5 + (i)\phi_8$$

i.e.  $\psi_6 = \phi_1 - i\phi_4 - \phi_5 + i\phi_8$

The SALC's  $\psi_5$  and  $\psi_6$  may be combined so as to involve real coefficients.

$$\psi_5 = \psi_5' + \psi_6' = 2\phi_1 - 2\phi_5$$

$$\psi_6 = \frac{\psi_5' - \psi_6'}{i} = 2\phi_4 - 2\phi_8$$

The normalized SALC's are

$$\psi_5 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_5)$$

$$\psi_6 = \frac{1}{\sqrt{2}}(\phi_4 - \phi_8)$$

For the set 2, we have

$$\psi_7 = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$$

$$\psi_8 = \frac{1}{\sqrt{2}}(\phi_6 - \phi_7)$$

The molecular orbitals are obtained by mixing SALC's of appropriate symmetries.

**Formation of Molecular Orbitals**

**$A_{2u}$  Symmetry**  $\psi_{1,2} = C_1\psi_1 + C_2\psi_2$

**$B_{1u}$  Symmetry**  $\psi_{3,4} = C_3\psi_3 + C_4\psi_4$

**$E_g$  Symmetry**  $\psi_{5,6,7,8} = C_5\psi_5 + C_6\psi_6 + C_7\psi_7 + C_8\psi_8$

For the molecular orbitals  $\psi_{1,2}$  we have

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

where  $H_{11} = \langle \psi_1 | \hat{H} | \psi_1 \rangle = \frac{1}{4} [\langle (\phi_1 + \phi_4 + \phi_5 + \phi_8) | \hat{H} | (\phi_1 + \phi_4 + \phi_5 + \phi_8) \rangle]$

$$= \frac{1}{4} [\langle \phi_1 | \hat{H} | \phi_1 \rangle + \langle \phi_4 | \hat{H} | \phi_4 \rangle + \langle \phi_5 | \hat{H} | \phi_5 \rangle + \langle \phi_8 | \hat{H} | \phi_8 \rangle]$$

$$= \frac{1}{4}(\alpha + \alpha + \alpha + \alpha) = \alpha$$

$$H_{12} = \langle \psi_1 | \hat{H} | \psi_2 \rangle = \frac{1}{4} [\langle (\phi_1 + \phi_4 + \phi_5 + \phi_8) | \hat{H} | (\phi_2 + \phi_3 + \phi_6 + \phi_7) \rangle]$$

$$= \frac{1}{4} [\langle \phi_1 | \hat{H} | \phi_2 \rangle + \langle \phi_4 | \hat{H} | \phi_3 \rangle + \langle \phi_5 | \hat{H} | \phi_6 \rangle + \langle \phi_8 | \hat{H} | \phi_7 \rangle]$$

$$= \frac{1}{4}(\beta + \beta + \beta + \beta) = \beta$$

$$H_{21} = H_{12}$$

$$\begin{aligned}
 H_{22} &= \langle \psi_2 | \hat{H} | \psi_2 \rangle = \frac{1}{4} [ \langle (\phi_2 + \phi_3 + \phi_6 + \phi_7) | \hat{H} | (\phi_2 + \phi_3 + \phi_6 + \phi_7) \rangle ] \\
 &= \frac{1}{4} [ \langle \phi_2 | \hat{H} | \phi_2 \rangle + \langle \phi_2 | \hat{H} | \phi_3 \rangle + \langle \phi_2 | \hat{H} | \phi_6 \rangle + \langle \phi_2 | \hat{H} | \phi_7 \rangle + \langle \phi_3 | \hat{H} | \phi_2 \rangle \\
 &\quad + \langle \phi_3 | \hat{H} | \phi_3 \rangle + \langle \phi_3 | \hat{H} | \phi_6 \rangle + \langle \phi_3 | \hat{H} | \phi_7 \rangle + \langle \phi_6 | \hat{H} | \phi_2 \rangle + \langle \phi_6 | \hat{H} | \phi_3 \rangle + \langle \phi_6 | \hat{H} | \phi_7 \rangle \\
 &\quad + \langle \phi_7 | \hat{H} | \phi_2 \rangle + \langle \phi_7 | \hat{H} | \phi_3 \rangle + \langle \phi_7 | \hat{H} | \phi_6 \rangle + \langle \phi_7 | \hat{H} | \phi_7 \rangle ] \\
 &= \frac{1}{4} [ \alpha + \beta + \beta + \beta + \alpha + \beta + \beta + \alpha + \beta + \beta + \alpha ] \\
 &= \alpha + 2\beta
 \end{aligned}$$

With these, the secular determinant becomes

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha + 2\beta - E \end{vmatrix} = 0 \Rightarrow \begin{vmatrix} x & 1 \\ 1 & x + 2 \end{vmatrix} \text{ where } x = \frac{x - E}{\beta}$$

which gives

$$x(x+2) - 1 = 0 \quad \text{i.e.} \quad x^2 + 2x - 1 = 0 \Rightarrow x = -1 \pm \sqrt{2}$$

$$\text{Hence } \frac{\alpha - E_1}{\beta} = -1 - \sqrt{2} \Rightarrow E_1 = \alpha + 2.414\beta$$

$$\frac{\alpha - E_2}{\beta} = -1 + \sqrt{2} \Rightarrow E_2 = \alpha - 0.414\beta$$

For  $E_1 = \alpha + 2.414\beta$ , the secular equation  $C_1(H_{11} - E) + C_2H_{12} = 0$ , gives

$$C_1(-2.414)\beta + C_2\beta = 0 \Rightarrow C_1/C_2 = 1/2.414 = 0.414$$

From the normalization of MO, we get

$$C_1^2 + C_2^2 = 1 \Rightarrow (0.414C_2)^2 + C_2^2 = 1 \Rightarrow C_2 = 0.924$$

$$C_1 = (0.414)C_2 \Rightarrow (0.414)(0.924) = 0.382$$

The MO becomes

$$\psi_1 = C_1\psi_1 + C_2\psi_2$$

$$\begin{aligned}
 &= (0.382) \left[ \frac{1}{2} (\phi_1 + \phi_4 + \phi_5 + \phi_8) \right] + (0.924) \left[ \frac{1}{2} (\phi_2 + \phi_3 + \phi_6 + \phi_7) \right] \\
 &= 0.191(\phi_1 + \phi_4 + \phi_5 + \phi_8) + 0.462(\phi_2 + \phi_3 + \phi_6 + \phi_7)
 \end{aligned}$$

For  $E_2 = \alpha - 0.414\beta$ , we will get

$$\psi_2 = 0.289(\phi_1 + \phi_4 + \phi_5 + \phi_8) - 0.408(\phi_2 + \phi_3 + \phi_6 + \phi_7)$$

For the functions  $\psi_{3,4}$ , we have

$$\begin{vmatrix} H_{33} - E & H_{34} \\ H_{43} & H_{44} - E \end{vmatrix} = 0 \Rightarrow \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - 2\beta - E \end{vmatrix} = 0 \Rightarrow \begin{vmatrix} x & 1 \\ 1 & x - 2 \end{vmatrix} = 0$$

Molecular Orbitals

$\psi_{3,4}$

This gives  $x(x-2) - 1 = 0$  i.e.  $x^2 - 2x - 1 = 0 \Rightarrow x = 1 \pm \sqrt{2}$

$$\text{Hence, } \frac{\alpha - E_3}{\beta} = 1 - \sqrt{2} \Rightarrow E_3 = \alpha + 0.414\beta$$

$$\frac{\alpha - E_4}{\beta} = 1 + \sqrt{2} \Rightarrow E_4 = \alpha - 2.414\beta$$

For  $E_3 = \alpha + 0.414\beta$ , the secular equation  $C_3(H_{33} - E) + C_4H_{12} = 0$ , gives

$$C_3(-0.414\beta) + C_4\beta = 0 \Rightarrow C_3/C_4 = 1/0.414 = 2.414$$

From the normalization condition, we get

$$C_3^2 + C_4^2 = 1 \Rightarrow (2.414C_4)^2 + C_4^2 = 1 \Rightarrow C_4 = 0.383$$

$$C_3 = 2.414C_4 = (2.414)(0.383) = 0.924$$

$$\begin{aligned}
 \text{Hence, } \psi_3 &= 0.924 \left[ \frac{1}{2} (\phi_1 - \phi_4 + \phi_5 - \phi_8) \right] + 0.383 \left[ \frac{1}{2} (\phi_2 - \phi_3 + \phi_6 - \phi_7) \right] \\
 &= 0.462(\phi_1 - \phi_4 + \phi_5 - \phi_8) + 0.191(\phi_2 - \phi_3 + \phi_6 - \phi_7)
 \end{aligned}$$

For  $E_4 = \alpha - 2.414\beta$ , we will get

$$\psi_4 = 0.191(\phi_1 - \phi_4 + \phi_5 - \phi_8) - 0.462(\phi_2 - \phi_3 + \phi_6 - \phi_7)$$

For the molecular orbitals  $\psi_{5,6,7,8}$ , we have

$$\begin{vmatrix} H_{55} - E & H_{56} & H_{57} & H_{58} \\ H_{65} & H_{66} - E & H_{67} & H_{68} \\ H_{75} & H_{76} & H_{77} - E & H_{78} \\ H_{85} & H_{86} & H_{87} & H_{88} - E \end{vmatrix} = 0$$

$$\Rightarrow \begin{vmatrix} \alpha - E & 0 & \beta & 0 \\ 0 & \alpha - E & 0 & \beta \\ \beta & 0 & \alpha - E & 0 \\ 0 & \beta & 0 & \alpha - E \end{vmatrix} = 0$$

Carrying out the change  $R_2 \leftrightarrow R_3$  and then  $C_2 \leftrightarrow C_3$ , we get

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & 0 & 0 \\ 0 & 0 & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

This factors into

$$\begin{aligned}
 \psi_{5,7} &= C_5\psi_5 + C_7\psi_7 \\
 \psi_{6,8} &= C_6\psi_6 + C_8\psi_8
 \end{aligned}
 \quad \text{with } \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \Rightarrow \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

This gives  $x^2 - 1 = 0 \Rightarrow x = \pm 1$

Substituting in secular equation along with normalization of MO, we get

For  $x = -1$ ,  $E_5 = \alpha + \beta$ ;  $C_5 = C_7 = 1/\sqrt{2}$

For  $x = 1$ ,  $E_7 = \alpha - \beta$ ;  $C_5 = -C_7 = 1/\sqrt{2}$

Hence, the molecular orbitals are

For  $E_5 = \alpha + \beta$   $\psi_5 = \frac{1}{2}(\phi_1 - \phi_3 + \phi_2 - \phi_6)$

For  $E_6 = \alpha - \beta$   $\psi_7 = \frac{1}{2}(\phi_1 - \phi_3 - \phi_2 + \phi_6)$

For  $E_7 = \alpha + \beta$   $\psi_6 = \frac{1}{2}(\phi_4 - \phi_8 + \phi_3 - \phi_7)$

For  $E_8 = \alpha - \beta$   $\psi_8 = \frac{1}{2}(\phi_4 - \phi_8 - \phi_3 + \phi_7)$

Work out the Hückel  $\pi$ -molecular orbitals along with their energies for trivinylmethyl radical,  $\cdot\text{C}(\text{CH}=\text{CH}_2)_3$ .

The radical trivinylmethyl belongs to the point group  $D_{3h}$ . The numbering of atoms is shown in Fig. 5.21.3.

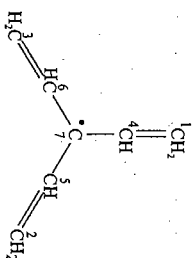


Fig. 5.21.3. Numbering of atoms in trivinylmethyl radical

### Free sets of $2p_z$ orbitals

Each of the seven carbon atoms contributes one  $2p_z$  orbital towards  $\pi$ -molecular orbitals. These orbitals may be classified into three sets—the orbitals in one set are not interchanged with any of the orbital in the other sets under the symmetry operations of the point group  $D_{3h}$ . The three sets are as follows.

- Set 1 Carbon atoms 1, 2 and 3
- Set 2 Carbon atoms 4, 5 and 6
- Set 3 Carbon atom 7

These three sets may be considered separately for the formation of SALC's.

Based on the  $2p_z$  orbitals in each set, the reducible representations are as follows.

$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$
$\Gamma_{\text{set1}}$	3	0	-1	-3	0	1
$\Gamma_{\text{set2}}$	3	0	-1	-3	0	1
$\Gamma_{\text{set3}}$	1	1	-1	-1	-1	1

### Irreducible Representations

The sets 1 and 2 have identical reducible representations and thus will include the same type and number of irreducible representations. Based on the expression

$$a_i = \frac{1}{h} \sum_C n_C \chi(C) \chi_i(C)$$

the irreducible representations are as follows.

$$a(A_2'') = \frac{1}{12} [1(3)(1) + 2(0)(1) + 3(-1)(-1) + 1(-3)(-1) + 2(0)(-1) + 3(1)(1)] = 1$$

$$a(E'') = \frac{1}{12} [1(3)(2) + 2(0)(-1) + 3(-1)(0) + 1(-3)(-2) + 2(0)(1) + 3(0)(1)] = 1$$

For the rest of representations,  $a = 0$ .

Hence,  $\Gamma_{\text{set1}} = A_2'' + E''$

$$\Gamma_{\text{set2}} = A_2'' + E''$$

$$\Gamma_{\text{set3}} = A_2''$$

The SALC's involving  $2p_z$  orbitals which form the bases of above irreducible representations may be generated by considering the symmetry operations of the group  $C_{3v}$ . We ignore multiplication factors as these are ascertained by normalization of SALC's.

$$\begin{aligned} \text{Set 1 } \hat{P}_A \phi_1 &= \chi(E) \hat{E} \phi_1 + \chi(C_3) \hat{C}_3 \phi_1 + \chi(C_3^2) \hat{C}_3^2 \phi_1 \\ &= (1) \phi_1 + 1(\phi_2) + 1(\phi_3) \end{aligned}$$

The normalized SALC is

$$\psi_1 = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3)$$

$$\text{Set 2 } \psi_2 = \frac{1}{\sqrt{3}}(\phi_4 + \phi_5 + \phi_6)$$

$$\text{Set 3 } \psi_3 = \phi_7$$

$$\text{Set 1 } \hat{P}_E \phi_1 = (1) \phi_1 + e \phi_2 + e^* \phi_3; \quad \text{where } e = \exp(2\pi i/3)$$

$$\text{i.e. } \psi_4 = \phi_1 + e \phi_2 + e^* \phi_3$$

$$\hat{P}_E \phi_1 = (1) \phi_1 + e^* \phi_2 + e \phi_3$$

$$\text{i.e. } \psi_5 = \phi_1 + e^* \phi_2 + e \phi_3$$

The SALC's  $\psi_4$  and  $\psi_5$  may be combined so as to give SALC's involving real coefficients.

$$\psi_4 = \psi_4' + \psi_5' = 2\phi_1 + (e + e^*)\phi_2 + (e + e^*)\phi_3$$

$$= 2\phi_1 + 2 \cos(2\pi/3) \{ \phi_2 + \phi_3 \}$$

$$= 2\phi_1 - \phi_2 - \phi_3$$

$$\psi_5 = \frac{\psi_4' - \psi_5'}{i} = 2 \sin(2\pi/3) \{ \phi_2 - \phi_3 \} = \sqrt{3}(\phi_2 - \phi_3)$$



The normalized SALC's are

$$\psi_4 = \frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3) \quad \text{and} \quad \psi_5 = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$$

Set 2  $\psi_6 = \frac{1}{\sqrt{6}}(2\phi_4 - \phi_5 - \phi_6)$  and  $\psi_7 = \frac{1}{\sqrt{2}}(\phi_5 - \phi_6)$

The molecular orbitals are obtained by mixing SALC's of appropriate symmetries.

$$\psi_{1,2,3} = C_1\psi_1 + C_2\psi_2 + C_3\psi_3$$

$$\psi_{4,5,6,7} = C_4\psi_4 + C_5\psi_5 + C_6\psi_6 + C_7\psi_7$$

For the molecular orbitals  $\psi_{1,2,3}$ , we have

$$\begin{vmatrix} H_{11} - E & H_{12} & H_{13} \\ H_{21} & H_{22} - E & H_{23} \\ H_{31} & H_{32} & H_{33} - E \end{vmatrix} = 0$$

$$\begin{aligned} \text{where } H_{11} &= \langle \psi_1 | \hat{H} | \psi_1 \rangle = \frac{1}{3} [\langle (\phi_1 + \phi_2 + \phi_3) | \hat{H} | (\phi_1 + \phi_2 + \phi_3) \rangle] \\ &= \frac{1}{3} [\langle \phi_1 | \hat{H} | \phi_1 \rangle + \langle \phi_2 | \hat{H} | \phi_2 \rangle + \langle \phi_3 | \hat{H} | \phi_3 \rangle] \\ &= \frac{1}{3}(\alpha + \alpha + \alpha) = \alpha \end{aligned}$$

$$\begin{aligned} H_{12} &= \langle \psi_1 | \hat{H} | \psi_2 \rangle = \frac{1}{3} [\langle (\phi_1 + \phi_2 + \phi_3) | \hat{H} | (\phi_4 + \phi_5 + \phi_6) \rangle] \\ &= \frac{1}{3} [\langle \phi_1 | \hat{H} | \phi_4 \rangle + \langle \phi_2 | \hat{H} | \phi_5 \rangle + \langle \phi_3 | \hat{H} | \phi_6 \rangle] \\ &= \frac{1}{3}(\beta + \beta + \beta) = \beta \end{aligned}$$

$$\begin{aligned} H_{13} &= \langle \psi_1 | \hat{H} | \psi_3 \rangle = \frac{1}{\sqrt{3}} [\langle (\phi_1 + \phi_2 + \phi_3) | \hat{H} | \phi_7 \rangle] \\ &= 0 \end{aligned}$$

$$H_{21} = H_{12} = \beta$$

$$\begin{aligned} H_{22} &= \langle \psi_2 | \hat{H} | \psi_2 \rangle = \frac{1}{\sqrt{3}} [\langle (\phi_4 + \phi_5 + \phi_6) | \hat{H} | (\phi_4 + \phi_5 + \phi_6) \rangle] \\ &= \frac{1}{3} [\langle \phi_4 | \hat{H} | \phi_4 \rangle + \langle \phi_5 | \hat{H} | \phi_5 \rangle + \langle \phi_6 | \hat{H} | \phi_6 \rangle] \\ &= \frac{1}{3}(\alpha + \alpha + \alpha) = \alpha \end{aligned}$$

$$H_{23} = \langle \psi_2 | \hat{H} | \psi_3 \rangle = \frac{1}{\sqrt{3}} [\langle (\phi_4 + \phi_5 + \phi_6) | \hat{H} | \phi_7 \rangle]$$

$$\begin{aligned} &= \frac{1}{\sqrt{3}} [\langle \phi_4 | \hat{H} | \phi_7 \rangle + \langle \phi_5 | \hat{H} | \phi_7 \rangle + \langle \phi_6 | \hat{H} | \phi_7 \rangle] \\ &= \frac{1}{\sqrt{3}}(\beta + \beta + \beta) = \sqrt{3}\beta \end{aligned}$$

## Formation of Molecular Orbitals

### Molecular Orbitals

$\psi_{1,2,3}$

$$H_{31} = H_{13} = 0$$

$$H_{32} = H_{23} = \sqrt{3}\beta$$

$$H_{33} = \langle \psi_3 | \hat{H} | \psi_3 \rangle = \langle \phi_7 | \hat{H} | \phi_7 \rangle = \alpha$$

With these, the secular determinant becomes

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \sqrt{3}\beta \\ 0 & \sqrt{3}\beta & \alpha - E \end{vmatrix} = 0 \Rightarrow \begin{vmatrix} x & 1 & 0 \\ 1 & x & \sqrt{3} \\ 0 & \sqrt{3} & x \end{vmatrix} = 0 \quad \text{where } x = \frac{\alpha - E}{\beta}$$

which gives  $x(x^2 - 3) - x = 0$  i.e.  $x = 0$ ,  $x = -2$  and  $x = 2$

These give  $E_1 = \alpha$ ,  $E_2 = \alpha + 2\beta$  and  $E_3 = \alpha - 2\beta$

The secular equations are

$$C_1(\alpha - E) + C_2\beta = 0$$

$$C_1\beta + C_2(\alpha - E) + C_3(\sqrt{3}\beta) = 0$$

$$C_2(\sqrt{3}\beta) + C_3(\alpha - E) = 0$$

These along with normalization expression

$$C_1^2 + C_2^2 + C_3^2 = 1$$

give the following MOs.

$$\psi_1 = \frac{1}{2}(\phi_1 + \phi_2 + \phi_3) - \frac{1}{2}\phi_7; \quad E_1 = \alpha$$

$$\psi_2 = \frac{1}{2\sqrt{6}}(\phi_1 + \phi_2 + \phi_3) + \frac{1}{\sqrt{6}}(\phi_4 + \phi_5 + \phi_6) + \frac{3}{2\sqrt{6}}\phi_7; \quad E_2 = \alpha + 2\beta$$

$$\psi_3 = \frac{1}{2\sqrt{6}}(\phi_1 + \phi_2 + \phi_3) - \frac{1}{\sqrt{6}}(\phi_4 + \phi_5 + \phi_6) + \frac{3}{2\sqrt{6}}\phi_7; \quad E_3 = \alpha - 2\beta$$

For molecular orbitals  $\psi_{4,5,6,7}$ , we will have

$$\begin{vmatrix} H_{44} - E & H_{45} & H_{46} & H_{47} \\ H_{54} & H_{55} - E & H_{56} & H_{57} \\ H_{64} & H_{65} & H_{66} - E & H_{67} \\ H_{74} & H_{75} & H_{76} & H_{77} - E \end{vmatrix} = 0$$

$$\Rightarrow \begin{vmatrix} \alpha - E & 0 & \beta & 0 \\ 0 & \alpha - E & 0 & \beta \\ \beta & 0 & \alpha - E & 0 \\ 0 & \beta & 0 & \alpha - E \end{vmatrix} = 0$$

Carrying out the change  $R_2 \leftrightarrow R_3$  followed by  $C_2 \leftrightarrow C_3$ , we get

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & 0 & 0 \\ 0 & 0 & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

The above secular determinant leads to the following combinations.

$$\psi_{4,6} = C_4\psi_4 + C_6\psi_6$$

$$\psi_{5,7} = C_5\psi_5 + C_7\psi_7$$

For both these combinations, the secular determinant is

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \quad \text{i.e.} \quad \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

Opening the secular determinant, we get

$$x^2 - 1 = 0 \Rightarrow x = -1 \quad \text{and} \quad x = 1$$

These give

$$E_4 = \alpha + \beta \quad \text{and} \quad E_6 = \alpha - \beta$$

$$E_5 = \alpha + \beta \quad \text{and} \quad E_7 = \alpha - \beta$$

Substituting these in the secular equation  $C_4(\alpha - E) + C_6\beta = 0$  [or  $C_5(\alpha - E) + C_7\beta = 0$ ] along with the normalization expression  $C_4^2 + C_6^2 = 1$  (or  $C_5^2 + C_7^2 = 1$ ) give the following results.

$$\psi_4 = \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3) + \frac{1}{\sqrt{12}}(2\phi_4 - \phi_5 - \phi_6); \quad E_4 = \alpha + \beta$$

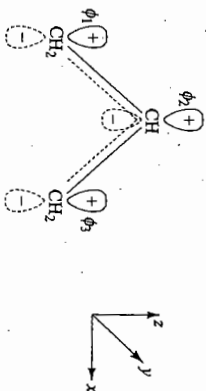
$$\psi_5 = \frac{1}{2}(\phi_2 - \phi_3) + \frac{1}{2}(\phi_5 - \phi_6); \quad E_5 = \alpha + \beta$$

$$\psi_6 = \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3) - \frac{1}{\sqrt{12}}(2\phi_4 - \phi_5 - \phi_6); \quad E_6 = \alpha - \beta$$

$$\psi_7 = \frac{1}{2}(\phi_2 - \phi_3) - \frac{1}{2}(\phi_5 - \phi_6); \quad E_7 = \alpha - \beta$$

Work out  $\pi$ -molecular orbitals of an allyl radical along with their energies.

The allyl radical is shown in Fig. 5.21.4. All the three carbon atoms lie in the  $xy$  plane. The  $p_z$  orbital on each carbon atom lies along the  $z$ -direction. The molecule belongs to the group  $C_{2v}$  with  $C_2$  axis coinciding with  $y$ -direction.



The reducible representation based on the three  $p_z$  orbital is

$$\begin{array}{c|ccc} C_{2v} & E & C_2 & \sigma_y & \sigma_{xz} \\ \hline \Gamma_{p_z} & 3 & -1 & 1 & -3 \end{array}$$

The reduction of reducible representation gives

$$a(A_2) = \frac{1}{h} [\chi(E)\chi_i(E) + \chi(C_2)\chi_i(C_2) + \chi(\sigma_y)\chi_i(\sigma_y) + \chi(\sigma_{xz})\chi_i(\sigma_{xz})]$$

$$= \frac{1}{4} [(1)(3) + (1)(-1) + (-1)(1) + (-1)(-3)] = 1$$

$$a(B_1) = \frac{1}{4} [(1)(3) + (-1)(-1) + (1)(1) + (-1)(-3)] = 2$$

$$\text{Hence} \quad \Gamma_{p_z} = A_2 + 2B_1$$

### Formation of SALC's

The use of projection operator gives the following SALC's.

$$\hat{P}_{B_1}\phi_1 = \chi_{B_1}(E) \{ \hat{E}\phi_1 \} + \chi_{B_1}(C_2) \{ \hat{C}_2\phi_1 \} + \chi_{B_1}(\sigma_y) \{ \hat{\sigma}_{yz}\phi_1 \} + \chi_{B_1}(\sigma_{xz}) \{ \hat{\sigma}_{xz}\phi_1 \}$$

$$= (1)\phi_1 + (-1)(-\phi_3) + (1)(\phi_3) + (-1)(-\phi_1)$$

$$= 2\phi_1 + 2\phi_3$$

The normalized function is  $\psi_1^{(B_1)} = \frac{1}{\sqrt{2}}(\phi_1 + \phi_3)$

$$\hat{P}_{B_2}\phi_2 = (1)(\phi_2) + (-1)(-\phi_2) + (1)(\phi_2) + (-1)(-\phi_2) = 4\phi_2$$

that is  $\psi_2^{(B_2)} = \phi_2$

$$\hat{P}_{A_2}\phi_1 = (1)\phi_1 + (1)(-\phi_3) + (-1)(\phi_3) + (-1)(-\phi_1)$$

$$= 2\phi_1 - 2\phi_3$$

The normalized function is  $\psi_3^{(A_2)} = \frac{1}{\sqrt{2}}(\phi_1 - \phi_3)$

Since  $\psi_1$  and  $\psi_2$  are of same symmetry, we may write

$$\psi_{1,2} = C_1\psi_1 + C_2\psi_2$$

The secular determinant is

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

$$\text{where} \quad H_{11} = \langle \psi_1 | H_{op} | \psi_1 \rangle = \frac{1}{2} [\langle (\phi_1 + \phi_3) | H_{op} | (\phi_1 + \phi_3) \rangle]$$

$$= \frac{1}{2} [\langle \phi_1 | H_{op} | \phi_1 \rangle + \langle \phi_1 | H_{op} | \phi_3 \rangle + \langle \phi_3 | H_{op} | \phi_1 \rangle + \langle \phi_3 | H_{op} | \phi_3 \rangle]$$

$$= \frac{1}{2} [\alpha + 0 + 0 + \alpha] = \alpha$$

$$H_{12} = \langle \psi_1 | H_{op} | \psi_2 \rangle = \frac{1}{\sqrt{2}} [\langle (\phi_1 + \phi_3) | H_{op} | \phi_2 \rangle]$$

$$= \frac{1}{\sqrt{2}} [\langle \phi_1 | H_{op} | \phi_2 \rangle + \langle \phi_3 | H_{op} | \phi_2 \rangle]$$

$$= \frac{1}{\sqrt{2}} (\beta + \beta) = \sqrt{2}\beta$$

$$\text{Hence} \quad \begin{vmatrix} \alpha - E & \sqrt{2}\beta \\ \sqrt{2}\beta & \alpha - E \end{vmatrix} = 0 \quad \text{i.e.} \quad \begin{vmatrix} x & \sqrt{2} \\ \sqrt{2} & x \end{vmatrix} = 0 \quad \text{where } x = (\alpha - E)/\beta$$

$$\text{This gives} \quad x^2 - 2 = 0 \quad \text{or} \quad x = \pm\sqrt{2}$$

$$\text{For} \quad x = -\sqrt{2}, \quad E_1 = \alpha + \sqrt{2}\beta$$

$$\text{and for} \quad x = \sqrt{2}, \quad E_2 = \alpha - \sqrt{2}\beta$$

The secular equations are

$$\begin{aligned} C_1(H_{11} - E) + C_2 H_{12} &= 0 \\ C_1 H_{21} + C_2(H_{22} - E) &= 0 \end{aligned}$$

For  $E_1 = \alpha + \sqrt{2}\beta$ , we get  $C_1 = C_2$   
 $E_2 = \alpha - \sqrt{2}\beta$ ; we get  $C_1 = -C_2$

From the normalization expression ( $C_1^2 + C_2^2 = 1$ ) of molecular orbital, we get

$$\begin{aligned} E_1 = \alpha + \sqrt{2}\beta; \quad C_1 = C_2 = 1/\sqrt{2} \\ E_2 = \alpha - \sqrt{2}\beta; \quad C_1 = -C_2 = 1/\sqrt{2} \end{aligned}$$

Hence  $\psi_1 = \frac{1}{\sqrt{2}}\psi'_1 + \frac{1}{\sqrt{2}}\psi'_2 = \frac{1}{2}(\phi_1 + \sqrt{2}\phi_2 + \phi_3); \quad E_1 = \alpha + \sqrt{2}\beta$

$$\psi_2 = \frac{1}{\sqrt{2}}\psi'_1 - \frac{1}{\sqrt{2}}\psi'_2 = \frac{1}{2}(\phi_1 - \sqrt{2}\phi_2 + \phi_3); \quad E_2 = \alpha - \sqrt{2}\beta$$

The energy of  $\psi_3$  is

$$\begin{aligned} E_3 &= \langle \psi_3 | H_{op} | \psi_3 \rangle = \frac{1}{2} \langle (\phi_1 - \phi_3) | H_{op} | (\phi_1 - \phi_3) \rangle \\ &= \frac{1}{2} [\langle \phi_1 | H_{op} | \phi_1 \rangle - \langle \phi_1 | H_{op} | \phi_3 \rangle - \langle \phi_3 | H_{op} | \phi_1 \rangle + \langle \phi_3 | H_{op} | \phi_3 \rangle] \\ &= \frac{1}{2} [\alpha - 0 - 0 + \alpha] = \alpha \end{aligned}$$

## 5.22 IRREDUCIBLE REPRESENTATIONS OF VIBRATIONAL MOTIONS

**Degrees of Freedom** A system consisting of  $N$  atoms can be described by specifying three coordinates for each atom, i.e. a total of  $3N$  coordinates. Since any one of these components can vary by any amount, the system is said to possess  $3N$  independent components of motion or degrees of freedom. If  $N$  atoms are bound to form a molecule, the  $3N$  degrees of freedom can be reallocated as described in the following.

**Translational Motion** The translational motion can be described by stating  $x$ -,  $y$ - and  $z$ -coordinates of the centre of mass of the molecule. Thus, 3 degrees of freedom are used to describe the translational motion of a molecule.

**Rotational Motion** The rotational motion can be described by stating two angles along the two axes (excluding molecular axis) for a linear molecule and three angles along the three axes for a nonlinear molecule. Thus, 2 degrees of freedom for a linear molecule and 3 degrees of freedom for a nonlinear molecule are used to describe the rotational motion of a molecule.

**Vibrational Motion** The remaining degrees of freedom ( $3N-5$  for a linear molecule and  $3N-6$  for a nonlinear molecule) are used to describe the vibrational motion of a molecule. In other words, a molecule has  $3N-5$  (for a linear molecule) or  $3N-6$  (for a nonlinear molecule) independent modes of vibrations. These can be described in terms of internal displacement vectors representing changes in bond lengths and bond angles of a molecule.

## Irreducible Representations of Vibrational Motions

The irreducible representations for which vibrational motions form the bases are determined indirectly as described in the following.

Reducible representations based on the three mutually perpendicular vectors attached to each atom is determined. This is resolved into irreducible representations. From these, irreducible representations of translational and rotational motions as determined from the character table are deleted. The remaining irreducible representations correspond to the vibrational motions of the molecule.

### Example of Water Molecule

Water molecule (point group  $C_{2v}$ ) has a total of nine ( $= 3N$ ) degrees of freedom of which three ( $= 3N-6$ ) belongs to vibrational motions. As deduced earlier (Eq. 5.16.1), we have

$$\Gamma_{3N} = 3A_1 + A_2 + 2B_1 + 3B_2 \quad (\text{a total of 9 representations})$$

From the character table of  $C_{2v}$ , we find that

$$\Gamma_{\text{trans}} = B_1 + B_2 + A_1 \quad (\text{a total of 3 representations})$$

$$\Gamma_{\text{rot}} = B_2 + B_1 + A_2 \quad (\text{a total of 3 representations})$$

$$\begin{aligned} \text{Hence } \Gamma_{\text{vib}} &= \Gamma_{3N} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}} \\ &= 2A_1 + B_2 \end{aligned} \quad (\text{a total of 3 representations})$$

The above representations may be attributed to different modes of vibration involving changes in the internal coordinates, namely, bond lengths and bond angles.

Bond-stretching vibrations may be analysed by associating each bond with the change in bond-stretching vector. Reducible representation based on these vectors is established and is resolved into irreducible representations of the point group. The results are as follows.

$C_{2v}$	$E$	$C_2$	$\sigma_v(1)$	$\sigma_v(2)$	Comments
$\Gamma_{\text{stretch}}$	2	0	0	2	$C_2$ and $\sigma_v(1)$ interchange the two vectors, while $E$ and $\sigma_v(2)$ leave both unshifted

$$\alpha(A_1) = \frac{1}{4} [1(2)(1) + 1(0)(1) + 1(0)(1) + 1(2)(1)] = 1$$

$$\alpha(B_2) = \frac{1}{4} [1(2)(1) + 1(0)(-1) + 1(0)(-1) + 1(2)(1)] = 1$$

$$\text{Hence } \Gamma_{\text{stretch}} = A_1 + B_2$$

Thus, two modes of vibration belong to bond-stretching vibrations with irreducible representations  $A_1$  and  $B_2$ , respectively.

Angle-deforming vibrations may be analysed in terms of change in bond angles as the bases. The vector used is the change in angle  $\Delta\theta$  which undergoes deformation. Reducible representation with this vector as a basis is

### Angle-Deforming Vibrations



$C_{3v}$	$E$	$C_2$	$\sigma_v(1)$	$\sigma_v(2)$	Comments
$\Gamma_{\text{angle}}$	1	1	1	1	In each operation, bond angle remains unshifted.

These characters are those of the  $A_1$  irreducible representation. This also follows from the expression  $\Gamma_{\text{vib}} - \Gamma_{\text{stretch}}$

**Example of  $\text{NH}_3$  Molecule**  
Ammonia (point group  $C_{3v}$ ) has a total of twelve ( $= 3N$ ,  $N = 4$ ) degrees of freedom of which six ( $= 3N - 6$ ) belongs to vibrational motions. As deduced earlier (Eq. 5.16.2), we have

$$\Gamma_{3N} = 3A_1 + A_2 + 4E \quad (\text{a total of 12 representations})$$

From the character table of  $C_{3v}$ , we find that

$$\Gamma_{\text{trans}} = E + A_1 \quad (\text{a total of 3 representations})$$

$$\Gamma_{\text{rot}} = E + A_2 \quad (\text{a total of 3 representations})$$

$$\begin{aligned} \text{Hence } \Gamma_{\text{vib}} &= \Gamma_{3N} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}} \\ &= 2A_1 + 2E \end{aligned} \quad (\text{a total of 6 representations})$$

**Bond-Stretching Vibrations**  
Reducible representation for which changes in bond-stretching vectors form the bases is

$C_{3v}$	$E$	$2C_2$	$3\sigma_v$	Comments
$\Gamma_{\text{stretch}}$	3	0	1	$E$ interchanges no bond vector, $C_2$ and $C_3$ change all the three vectors and each of three $\sigma_v$ operation leaves one bond unshifted.

This is resolved as

$$\Gamma_{\text{stretch}} = A_1 + E \quad (\text{a total of 3 representations})$$

**Angle-Deforming Vibrations**  
There are three angle-deforming vectors  $\Delta\theta_1$ ,  $\Delta\theta_2$  and  $\Delta\theta_3$ . Based on these, the reducible representation is

$C_{3v}$	$E$	$2C_2$	$3\sigma_v$	Comments
$\Gamma_{\text{angle}}$	3	0	1	$E$ interchanges no bond angle, $C_2$ and $C_3$ shift all the three angles and each of three $\sigma_v$ operation leaves one angle unshifted.

This is resolved as

$$\Gamma_{\text{angle}} = A_1 + E \quad (\text{a total of 3 representations})$$

**Example of  $\text{CH}_4$  Molecule**  
Methane (point group  $T_d$ ) has a total of fifteen ( $= 3N$ ) degrees of freedom of which nine ( $= 3N - 6$ ) belong to vibrational motions. As deduced earlier (Eq. 5.16.3), we have

$$\Gamma_{3N} = A_1 + E + T_1 + 3T_2 \quad (\text{a total of 15 representations})$$

### Bond-Stretching Vibrations

From the character table of  $T_d$ , we have

$$\Gamma_{\text{trans}} = T_2 \quad (\text{a total of 3 representations})$$

$$\Gamma_{\text{rot}} = T_1 \quad (\text{a total of 3 representations})$$

$$\begin{aligned} \text{Hence } \Gamma_{\text{vib}} &= \Gamma_{3N} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}} \\ &= A_1 + E + 2T_2 \end{aligned} \quad (\text{a total of 9 representations})$$

Reducible representation for which changes in bond-stretching vectors form the bases is

$T_d$	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\Gamma_{\text{stretch}}$	4	1	0	0	2

This is resolved as

$$\Gamma_{\text{stretch}} = A_1 + T_2 \quad (\text{a total of four representations})$$

There are six angle-deforming vectors ( $\text{H}_a\text{CH}_b$ ,  $\text{H}_b\text{CH}_c$ ,  $\text{H}_c\text{CH}_d$ ,  $\text{H}_d\text{CH}_a$ ,  $\text{H}_b\text{CH}_d$ ,  $\text{H}_c\text{CH}_a$ ). Based on these, the reducible representation is

$T_d$	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\Gamma_{\text{angle}}$	6	0	0	2	2

This is resolved as

$$\Gamma_{\text{angle}} = A_1 + E + T_2 \quad (\text{a total of six representations})$$

**Redundant Representation** If we count the number of representations in  $\Gamma_{\text{stretch}}$  and  $\Gamma_{\text{angle}}$ , we find that there are ten ( $= 4 + 6$ ) representations, i.e. there are ten independent modes of vibration—one extra than the required modes of vibration. We find that

$$\begin{aligned} \Gamma_{\text{stretch}} + \Gamma_{\text{angle}} &= (A_1 + T_2) + (A_1 + E + T_2) \\ &= 2A_1 + E + 2T_2 \end{aligned} \quad (\text{Eqs.})$$

Comparing this with

$$\Gamma_{\text{vib}} = A_1 + E + 2T_2 \quad (\text{Eq.})$$

we find that the representation  $A_1$  is extra. This is called the *spurious* or *redundant representation*. Which of the two  $A_1$  representations (whether in  $\Gamma_{\text{stretch}}$  or  $\Gamma_{\text{angle}}$ ) is redundant representation can be easily identified based on the following facts.

There are four bonds in  $\text{CH}_4$  molecule and each of these can undergo a change in bond length independently of the others. But the six angles in  $\text{CH}_4$  cannot be independently changed. If any five are arbitrarily changed, the change in the sixth angle is automatically fixed. In the  $A_1$  representation of  $\Gamma_{\text{angle}}$ , all the six angles have to be changed in identical manner (either increase or decrease) at the same time which is not possible. Hence, the  $A_1$  representation in  $\Gamma_{\text{angle}}$  is redundant. Thus, the correct list of representations is

$$\begin{aligned} \Gamma_{\text{stretch}} &= A_1 + T_2 \\ \Gamma_{\text{angle}} &= E + T_2 \end{aligned}$$

From this, it may be concluded that

- (i) The representation  $A_1$  consists of purely bond stretching, i.e. only bond distances are changed.
- (ii) The representation  $E$  consists of purely bond-angles deformation.
- (iii) The representations  $T_2$  which occur in both  $\Gamma_{\text{stretch}}$  and  $\Gamma_{\text{angle}}$  involve both bond stretching and angles deformation.

### Example of $\text{CH}_3\text{D}$

The molecule  $\text{CH}_3\text{D}$  belongs to the point group  $C_{3v}$ . It has a total of 15 ( $= 3N$ ,  $N=5$ ) degrees of freedom of which 9 ( $= 3N-6$ ) belongs to the vibrational motions. The reducible representation based on the three vectors on each atom is

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$
$\Gamma_{3N}$	15	0	3

The resolution of this representation gives

$$\Gamma_{3N} = 4A_1 + A_2 + 5E$$

From the character table, we find that

$$\Gamma_{\text{trans}} = A_1 + E$$

$$\Gamma_{\text{rot}} = A_2 + E$$

$$\text{Hence } \Gamma_{\text{vib}} = \Gamma_{3N} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}} = 3A_1 + 3E$$

The reducible representation based on the changes in bond-stretching vectors is

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$
$\Gamma_{\text{stretch}}$	4	1	2

Its resolution gives

$$\Gamma_{\text{stretch}} = 2A_1 + E$$

The reducible representation based on angle-deforming vectors is

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$
$\Gamma_{\text{angle}}$	6	0	2

$$\text{Its resolution is } \Gamma_{\text{angle}} = 2A_1 + 2E$$

The  $A_1$  representation in  $\Gamma_{\text{angle}}$  is redundant six it is not possible to change all the six angles in identical manner.

$\text{Trans-N}_2\text{F}_2$  (point group  $C_{2h}$ ) has a total of twelve ( $= 3N$ ) degrees of freedom of which six ( $= 3N-6$ ) belong to vibrational motions. As deduced earlier (Eq. 5.16.4), we have

$$\Gamma_{3N} = 4A_g + 2B_g + 2A_u + 4B_u$$

From the character table of  $C_{2h}$ , we find that

$$\Gamma_{\text{trans}} = B_u + B_u + A_u$$

$$\Gamma_{\text{rot}} = B_g + B_g + A_g$$

### Bond-Stretching Vibrations

$$\text{Hence } \Gamma_{\text{vib}} = \Gamma_{3N} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}} = 3A_g + A_u + 2B_u$$

Reducible representation for which changes in bond-stretching vectors form the bases is

$C_{2h}$	$E$	$C_2$	$i$	$\sigma_h$
$\Gamma_{\text{stretch}}$	3	1	1	3

This is reduced to

$$\Gamma_{\text{stretch}} = 2A_g + B_u$$

There are two angle-deformation vectors in the molecular plane. Reducible representation for which these vectors form the bases is

$C_{2h}$	$E$	$C_2$	$i$	$\sigma_h$
$\Gamma_{\text{angle}}$	2	0	0	2

This is reduced to

$$\Gamma_{\text{angle}} = A_g + B_u$$

The only left-out representation is  $A_u$ . Inspection of this irreducible representation we find that the character of inversion operation is  $-1$ . This implies that this representation represents out-of-plane deformation.

## 5.23 PREDICTING PROBABILITY OF A SPECTRAL TRANSITION

The intensity of a spectral transition from a state  $\psi_i$  to a state  $\psi_j$  is directly proportional to the square of transition moment integral, defined as

$$T = \int \psi_i \hat{\mu} \psi_j d\tau \quad (5.23.1)$$

where  $\hat{\mu}$  is the operator for the electric-dipole of a molecule. Since the electric dipole is a vector quantity, the above integral may be expressed in terms of the following integrals.

$$T_x = \int \psi_i \hat{\mu}_x \psi_j d\tau; \quad T_y = \int \psi_i \hat{\mu}_y \psi_j d\tau \quad \text{and} \quad \int \psi_i \hat{\mu}_z \psi_j d\tau \quad (5.23.2)$$

The transition is said to be one-dimensionally polarized if any one of the three above integrals has a nonzero value while the other two have zero values.

In a molecule, if both  $x$  and  $y$  jointly form the bases of irreducible representation, the transition is said to be  $xy$  polarized provided  $T_x \neq 0$ ,  $T_y \neq 0$  and  $T_z = 0$ .

No polarization effect is observed if all the three coordinates form the bases of irreducible representation of a molecule.

The problem of predicting whether a certain transition is allowed or not depends on the nonzero value(s) of the above three integrals. The guiding principle for this fact may be understood from the following analysis.

Each transition moment integral, i.e.  $\langle \psi_f | \hat{\mu} | \psi_i \rangle$ , is a number and is therefore invariant under all the operations of the group to which the molecule belongs. Hence, all operations on the transition moment integral should leave it unchanged, i.e.

$$\hat{R}(\psi_f | \hat{\mu} | \psi_i) = (+1) \langle \psi_f | \hat{\mu} | \psi_i \rangle$$

The above condition is satisfied only if the integrand of transition moment integral transforms as the totally symmetric representation of the group concerned. In other words, for the transition  $\psi_i \rightarrow \psi_f$  to be allowed, the direct product of representations of  $\psi_i$ ,  $\psi_f$  and  $\hat{\mu}$  (which implies the multiplication of the corresponding characters of operations of the involved representations) should correspond to the totally symmetric representation.

Alternatively, it may be stated as follows. The direct product of the representations of the two states  $\psi_i$  and  $\psi_f$  should correspond to the irreducible representation to which  $x$ ,  $y$ , or  $z$ , respectively, belongs.

For the fundamental transition in the  $i$ th normal mode of vibration, Eq. (5.23.2) takes the form

$$\int \psi_0 | \hat{\mu}_x | \psi_i d\tau$$

$$\int \psi_0 | \hat{\mu}_y | \psi_i d\tau$$

$$\int \psi_0 | \hat{\mu}_z | \psi_i d\tau$$

where  $\psi_0$  is the vibrational ground wave function and  $\psi_i$  is the vibrational first excited wave function. It is known that

- (i) The vibrational ground wave function is totally symmetric.
- (ii) The symmetry properties of the component of the dipole moment are the same as those of a translational vector along the same axis.
- (iii) The symmetric properties of the first excited vibrational wave function are the same as those of irreducible representation of the normal mode of vibration.

In order that the direct product of  $\psi_0$ ,  $\hat{\mu}_i$  and  $\psi_i$  belongs to the totally symmetric representation, both  $\hat{\mu}_i$  and  $\psi_i$  should belong to the same representation.

Thus the essential criterion for observing fundamental transition in the infrared spectroscopy is

*A fundamental transition will be infrared active if the normal mode which is excited belongs to the same representation as any one or several of the Cartesian coordinates.*

The symmetry selection rule for Raman spectra is derived from the integral

$$\int \psi_0 | \alpha | \hat{\psi}_i d\tau \quad (5.23.3)$$

where  $\alpha$  is the polarizability of the molecule. The polarizability  $\alpha$  is a tensor, it has a  $3 \times 3$  array of components

$$\begin{vmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{vmatrix} \quad (5.23.4)$$

For vibrational transitions  $\alpha_{ij} = \alpha_{ji}$  (where  $i, j = x, y$  or  $z$ ), and thus there are six distinct components, namely,  $\alpha_x$ ,  $\alpha_y$ ,  $\alpha_z$ ,  $\alpha_{xy}$ ,  $\alpha_{yz}$  and  $\alpha_{zx}$ . These are transformed by the symmetry operations in the same way as  $x^2$ ,  $y^2$ ,  $z^2$ ,  $xy$ ,  $xz$  and  $yz$ , respectively. The six polarizability functions generate a reducible representation which can be resolved into irreducible representations involving the above combination of coordinates.

In order that Eq. (5.23.3) is nonzero with any of the six components, we must have *A fundamental transition will be Raman active if the normal mode involved belongs to the same irreducible representation as one or more of the components of the polarizability tensor of the molecule.*

## ILLUSTRATIONS OF IR AND RAMAN SPECTRA

### Water Molecule

Water belongs to the point group  $C_{2v}$ . From its character table, we find that Stretching vibration  $A_1$  includes  $z$ ,  $x^2$ ,  $y^2$  and  $z^2$ . Thus it is active in both infrared and Raman spectra

Stretching vibration  $B_2$  includes  $y$  and  $yz$ . Thus, it is active in both infrared and Raman spectra

Bond-deformation vibration  $A_1$  is also active in both infrared and Raman spectra.

Ammonia belongs to the point group  $C_{3v}$ . From its character table, we find that Stretching vibration  $A_1$  includes  $z$ ,  $x^2 + y^2$  and  $z^2$ . Thus, it is active in both infrared and Raman spectra

Stretching vibration  $E$  includes  $x$ ,  $y$ ,  $xz$  and  $yz$ . Thus, it is active in both infrared and Raman spectra.

Bond-deformation vibrations also belong to  $A$  and  $E$  representations and thus both will be active in both infrared and Raman spectra.

### Trans $N_2F_2$

Trans  $N_2F_2$  belongs to the point group  $C_{2h}$ . From its character table, we find that Stretching vibrations  $A_g$  includes  $x^2$ ,  $y^2$  and  $xy$ . Thus, these modes are infrared inactive and Raman active.

Stretching vibration  $B_u$  involves  $x$  and  $y$ . Thus, this mode is infrared active and Raman inactive.

Likewise bending modes  $A_g$  and  $B_u$  are respectively, infrared inactive and Raman active.

Bending mode  $A_u$  involves only  $z$ . Thus, this mode is infrared active and Raman inactive.

**Ethane Molecule**

Methane belongs to the group  $T_d$ . From its character table we find that the bonding stretching vibration of  $A_1$  representation is IR inactive and Raman active.

Bond deformation vibration of E representation is also IR inactive and Raman active.

The stretching and bond deformation vibrations of  $T_2$  representation are active in both IR and Raman spectra.

The representation  $A_1$  includes  $z, x^2 + y^2$  and  $z^2$ . Thus, the three non-degenerate fundamental vibrations are both infrared and Raman active.

The representation E includes  $(x, y), (x^2 - y^2, xy)$  and  $(xz, yz)$ . Thus, the doubly degenerate fundamental vibrations are also both infrared and Raman active.

For a molecule having centre of symmetry, we have the following facts.

- The representations generated by the Cartesian coordinates  $x, y$  or  $z$  belong to u representations as the values of  $x, y$  and  $z$  change sign on inversion through the centre of symmetry. Since the dipole moment is ungerade and involves Cartesian coordinates, it follows that all vibrational modes belonging to u representations will be infrared active.
- The representations generated by binary products of two Cartesian coordinates (say,  $xy, xz, yz, x^2, y^2$  and  $z^2$ ) belong to g representations as these do not change sign on inversion through the centre of symmetry. Since the polarizability tensor involves binary products of Cartesian coordinates, it follows that all vibrational modes belonging to g representations will be Raman active.

The above fact, known in the form exclusion rule, is stated as follows.

*In a centrosymmetric molecule no Raman-active vibration is infrared active and vice versa.*

**ANALYSIS OF VIBRATIONAL MODES OF A LINEAR MOLECULE**

A linear molecule (point groups  $C_{\infty v}$  and  $D_{\infty h}$ ) involves an infinite number of symmetry operations. It is not possible to resolve a reducible representation into irreducible representations as  $h = \infty$ . It is, therefore, necessary to carry out the resolution by inspection.

Taking an example of  $CO_2$  (point group  $D_{\infty h}$ ) with the molecular axis as the  $z$ -axis, the reducible representation based on rotating the molecule about the  $z$ -axis by an angle  $\varphi$  is

$D_{\infty h}$	E	$2C_{\infty}(\varphi)$	$\infty\sigma_v$	i	$2S_{\infty}(\varphi)$	$\infty C_2$
No. of unshifted atoms	3	3	3	1	1	1
$\Gamma$	9	$3(1 + 2 \cos \varphi)^\dagger$	3	-3	$(-1 + 2 \cos \varphi)$	-1

<sup>†</sup> The  $z$ -vector contributes 1 as it remains unshifted! Each of  $x$ - and  $y$ -vectors contributes  $\cos \varphi$  as the component of displaced vector along the original vector is  $\cos \varphi$ .

From the character table of  $D_{\infty h}$ , we find that

$D_{\infty h}$	E	$2C_{\infty}(\varphi)$	$\infty\sigma_v$	i	$2S_{\infty}(\varphi)$	$\infty C_2$	$T_z$ ( $T_x, T_y$ ) ( $R_x, R_y$ )
$\Sigma_g^+$	1	1	1	-1	-1	-1	0
$\Pi_u$	2	$2 \cos \varphi$	0	-2	$2 \cos \varphi$	0	0
$\Pi_g$	2	$2 \cos \varphi$	0	2	$-2 \cos \varphi$	0	0

Hence, the characters  $\Gamma_{\text{trans}} + \Gamma_{\text{rot}}$  are

	E	$2C_{\infty}(\varphi)$	$\infty\sigma_v$	i	$2S_{\infty}(\varphi)$	$\infty C_2$
$\Gamma_{\text{trans}} + \Gamma_{\text{rot}}$ $= \Sigma_g^+ + \Pi_u + \Pi_g$	5	$1 + 4 \cos \varphi$	1	-1	-1	-1

The characters  $\Gamma_{\text{vib}}$  are

	E	$2C_{\infty}(\varphi)$	$\infty\sigma_v$	i	$2S_{\infty}(\varphi)$	$\infty C_2$
$\Gamma_{\text{vib}} = \Gamma - (\Gamma_{\text{trans}} + \Gamma_{\text{rot}})$	4	$2 + 2 \cos \varphi$	2	-2	$2 \cos \varphi$	0

Inspection of the character table of  $D_{\infty h}$  reveals that  $\Gamma_{\text{vib}}$  is obtained by adding the following representations.

	E	$2C_{\infty}(\varphi)$	$\infty\sigma_v$	i	$2S_{\infty}(\varphi)$	$\infty C_2$
$\Sigma_g^+$	1	1	1	1	1	-1
$\Sigma_u^+$	1	1	1	-1	-1	-1
$\Pi_u$	2	$2 \cos \varphi$	0	-2	$2 \cos \varphi$	0

Hence  $\Gamma_{\text{vib}} = \Sigma_g^+ + \Sigma_u^+ + \Pi_u$

that is, there are two non-degenerate vibrations, one of which is totally symmetric and two doubly-degenerate vibrations.

Reducible representation based on the bond-stretching vectors ( $O \perp C \equiv O$ ) is

	E	$2C_{\infty}(\varphi)$	$\infty\sigma_v$	i	$2S_{\infty}(\varphi)$	$\infty C_2$
	2	2	2	0	0	0

which is obtained by adding irreducible representations  $\Sigma_g^+$  and  $\Sigma_u^+$ .

The bending vibrations correspond to the remaining representation  $\Pi_u$ .

The  $CO_2$  molecule a centrosymmetric molecule. The rule of mutual exclusion is followed by this molecule. The vibration  $\Sigma_g^+$  is IR inactive and Raman active. The vibrations  $\Sigma_u^+$  and  $\Pi_u$  are IR active and Raman inactive.

**Problem 5.23.1****Solution**

Work out the irreducible representations of acetylene. Indicate which one is IR or Raman active.

The acetylene molecule ( $H-C \equiv C-H$ ) is a linear molecule with centre of symmetry. It belongs to the group  $D_{\infty h}$ .

Taking the molecular axis as the  $z$ -axis, the reducible representation based on rotating the molecule about the  $z$ -axis by an angle  $\varphi$  is

$D_{\infty h}$	$E$	$2C_{\infty}(\phi)$	$\dots$	$\infty C_2$	$i$	$2S_{\infty}(\phi)$	$\dots$	$\infty C_2$
No. of unshifted atoms	4	4		4	0	0		0
$\Gamma$	12	$4(1 + 2 \cos \phi)$		4	0	0		0

From the character table of  $D_{\infty h}$ , we find that the reducible representation representing translational and rotational motion is

$$\begin{array}{c} \Gamma_{\text{trans}} + \Gamma_{\text{rot}} \\ = \Sigma_u^+ + \Pi_u + \Pi_g \end{array} \quad \begin{array}{c} E \\ 2C_{\infty}(\phi) \end{array} \dots \begin{array}{c} \infty C_2 \\ i \end{array} \begin{array}{c} 2S_{\infty}(\phi) \end{array} \dots \begin{array}{c} \infty C_2 \end{array}$$

The characters of  $\Gamma_{\text{vib}}$  are

$$\begin{array}{c} \Gamma_{\text{vib}} = \Gamma - (\Gamma_{\text{trans}} + \Gamma_{\text{rot}}) \end{array} \quad \begin{array}{c} E \\ 2C_{\infty}(\phi) \end{array} \dots \begin{array}{c} \infty C_2 \\ i \end{array} \begin{array}{c} 2S_{\infty}(\phi) \end{array} \dots \begin{array}{c} \infty C_2 \end{array}$$

Inspection of the character table of  $D_{\infty h}$  reveals that  $\Gamma_{\text{vib}}$  is obtained by adding the following representations.

$E$	$2C_{\infty}(\phi)$	$\dots$	$\infty C_2$	$i$	$2S_{\infty}(\phi)$	$\dots$	$\infty C_2$	
$\Sigma_g^+$	1	1	1	1	1	1	1	$x^2 + y^2, z^2$ (Raman active)
$\Sigma_g^-$	1	1	1	1	1	1	1	$x^2 + y^2, z^2$ (Raman active)
$\Sigma_u^+$	1	1	1	1	1	1	1	$z$ (IR active)
$\Sigma_u^-$	1	1	1	1	1	1	1	$z$ (IR active)
$\Pi_u$	2	$2 \cos \phi$	0	-2	$2 \cos \phi$	0	0	$(x, y)$ (IR active)
$\Pi_g$	2	$2 \cos \phi$	0	2	$-2 \cos \phi$	0	0	$(x, y)$ (Raman active)

There are three non-degenerate vibrations, two of which are totally symmetric and a pair of two doubly-degenerate vibrations.

Reducible representation based on the bond-stretching vectors ( $H \overset{\text{L}}{\underset{\text{C}}{\text{C}}} H$ ) is

$E$	$2C_{\infty}(\phi)$	$\dots$	$\infty C_2$	$i$	$2S_{\infty}(\phi)$	$\dots$	$\infty C_2$
3	3		3	1	1		1

which is obtained by adding irreducible representations

$$\Sigma_g^+, \Sigma_g^+ \text{ and } \Sigma_u^+$$

The bending vibrations correspond to the remaining representations  $\Pi_u$  and  $\Pi_g$ .

The vibration modes  $\Sigma_g^+$  are IR inactive and Raman active. These correspond to symmetrical stretching modes which do not involve change in dipole moment.

The vibration mode  $\Sigma_u^+$  is IR active and Raman inactive. This corresponds to unsymmetrical stretching mode which involves change in dipole moment.

The vibration modes  $\Pi_g$  involve symmetrical bending which do not involve change in dipole moment. These are IR inactive and Raman active. The vibration modes  $\Pi_u$  involve unsymmetrical bending which involve change in dipole moment and is IR active and Raman inactive.

### Electronic Transitions in an Atom

### ILLUSTRATIONS OF ELECTRONIC TRANSITIONS

The electronic transitions in an atom follow the following two selection rules.

**LaPorte's rule** Each component of dipole moment operator has odd (ungerade) parity. In order to obtain an even (gerade) parity, the direct product of the representations of the initial and final wave functions should be odd, since odd  $\times$  odd = even. This is possible if one of the wave functions is odd and the other even. This fact is known as LaPorte's rule which may be stated as follows.

*The electronic transition between states of the same parity are forbidden.*

For example, s-s, p-p, or d-d transitions are forbidden while s-p, p-d, or d-f transitions are allowed. LaPorte's rule expressed in the form of selection rule is  $\Delta l = \pm 1$ , where  $l$  is azimuthal quantum number.

**Spin selection rule** Since the dipole moment operator does not involve spin, we can integrate spin components of wave functions separately, in order to have nonzero value, the electron in both the initial and final wavefunctions should involve the same spin. Thus, the spin selection rule is  $\Delta S = 0$ .

While predicting the feasibility of electronic transitions in a molecule, it is desirable to work out with the symmetries of ground and excited electronic states of the molecule instead of involved orbitals in the electronic transition. The symmetry of electronic state of a molecule is determined by evaluating direct product of representations (which involves the multiplication of corresponding characters) of the involved molecular orbitals. For a singly-occupied molecular orbital, the symmetry is that of the molecular orbital itself. For a doubly-occupied molecular orbital, the direct product of the same two representations always yields a totally symmetric representation and thus may be ignored in evaluating the direct product of the state of the molecule.

The ground electronic state of water<sup>†</sup> (point group:  $C_{2v}$ ) is

$$(a_1)^2 (b_2)^2 (a_1)^2 (b_1)^2$$

Its symmetry is  $A_1$  as it involves doubly occupied molecular orbitals.

The two electronic excited states of the molecules are as follows.

- (i)  $(a_1)^2 (b_2)^2 (a_1)^2 (b_1) (a_1)$  Symmetry:  $(b_1)(a_1) = B_1$   
 (ii)  $(a_1)^2 (b_2)^2 (a_1)^2 (b_1) (b_2)$  Symmetry:  $(b_1)(b_2) = A_2$

The symmetries of components of transition moment integrals  $\langle \psi_i | \hat{\mu}_x | \psi_j \rangle$ ,  $\langle \psi_i | \hat{\mu}_y | \psi_j \rangle$  and  $\langle \psi_i | \hat{\mu}_z | \psi_j \rangle$  for these transitions are as follows.

•  $a_1 \leftarrow b_1$  transition

$$\begin{array}{l} x\text{-component: } A_1 \times B_1 \times B_1 = A_1 \\ y\text{-component: } A_1 \times B_2 \times B_1 = A_2 \\ z\text{-component: } A_1 \times A_1 \times B_1 = B_1 \end{array} \quad \begin{array}{l} \text{Since the } x\text{-components includes} \\ \text{a totally symmetric } A_1 \text{ representa-} \\ \text{tion, the transition is allowed.} \end{array}$$

<sup>†</sup> For a single-electron orbital, a lower case Mulliken symbol is used. The symmetry of electronic state of the molecule is represented by a capital letter.



•  $b_2 \leftarrow b_1$  transition.

x-component:  $A_1 \times B_1 \times A_2 = B_2$  Since a totally symmetric representation is absent, the transition is forbidden.  
 y-component:  $A_1 \times B_2 \times A_2 = B_1$   
 z-component:  $A_1 \times A_1 \times A_2 = A_2$

The ground electronic state of butadiene (point group:  $C_{2h}$ ) is

$$(a_u)^2 (b_g)^2 \quad \text{Symmetry: } a_g \times a_g = A_g$$

The four electronic excited states of the molecule are as follows.

$$(a_u)^2 (b_g) (a_u)^* \quad \text{Symmetry: } b_g \times a_u = B_u$$

$$(a_u)^2 (b_g) (b_g)^* \quad \text{Symmetry: } b_g \times b_g = A_g$$

$$(a_u) (b_g)^2 (a_u)^* \quad \text{Symmetry: } a_u \times a_u = A_g$$

$$(a_u) (b_g)^2 (b_g)^* \quad \text{Symmetry: } a_u \times b_g = B_u$$

The components of transition moment integrals for these transitions are as follows.

(i)  $a_u^* \leftarrow b_g$  and  $b_g^* \leftarrow a_u$  transitions

x-component  $A_g \times B_u \times B_u = A_g$  Since the x- and y-components involve a totally symmetric representation  $A_g$ , the transitions are allowed.  
 y-component  $A_g \times B_u \times B_u = A_g$   
 z-component  $A_g \times A_u \times B_u = B_g$

(ii)  $b_g^* \leftarrow b_g$  transition  $a_u^* \leftarrow a_u$  transitions

x-component  $A_g \times B_u \times A_g = B_u$  Since a totally symmetric representation is absent, the transitions are forbidden.  
 y-component  $A_g \times B_u \times A_g = B_u$   
 z-component  $A_g \times A_u \times A_g = A_u$

**Comment** From the above transitions, it follows that

$g \leftrightarrow u$  transitions are allowed

$g \leftrightarrow g$

$u \leftrightarrow u$  transitions are forbidden

In Sec. 5.19, we have worked out the  $\pi$ -molecular orbitals of benzene. These are as follows.

$$\Psi_1(a_{1g}) = \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$\Psi_2(e_{1g}) = \frac{1}{\sqrt{12}} (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 - \phi_6)$$

$$\Psi_3(e_{1g}) = \frac{1}{\sqrt{2}} (\phi_2 + \phi_3 - \phi_5 - \phi_6)$$

$$\Psi_4(e_{2u}) = \frac{1}{\sqrt{12}} (2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)$$

$$\Psi_5(e_{2u}) = \frac{1}{\sqrt{2}} (\phi_2 - \phi_3 + \phi_5 - \phi_6)$$

$$\Psi_6(b_{2g}) = \frac{1}{\sqrt{6}} (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

Under Hückel approximations, the energies of the above molecular orbitals can be worked out by using the expression  $\langle \psi | \hat{H} | \psi \rangle$ . Their energies are as follows.

$$E_1 = \alpha + 2\beta, \quad E_2 = E_3 = \alpha + \beta, \quad E_4 = E_5 = \alpha - \beta \quad \text{and} \quad E_6 = \alpha - 2\beta.$$

Since the benzene contains 6  $\pi$ -electrons, the ground state of benzene is

$$(a_{1g})^2 (e_{1g})^4 \quad \text{Symmetry: } A_{1g}$$

The electronic spectrum of benzene will involve transitions from the  $e_{1g}$  level to the  $e_{2u}$  and  $b_{2g}$  levels. However, the transition  $e_{1g} \rightarrow b_{2g}$  involves  $g \leftrightarrow g$  transition and thus is a forbidden transition.

The promotion of one electron from  $e_{1g}$  level to  $e_{2u}$  will lead to the excited state

$$(a_{2u})^2 (e_{1g})^3 (e_{2u})$$

To work out the symmetry of the excited state, we require the symmetry of  $(e_{1g})^3$ . The direct product  $E_{1g} \times E_{1g} \times E_{1g}$  does not give the correct result for the orbital symmetry. From quantum mechanics, it is found that the symmetry properties of  $(e_{1g})^3$  state is identical with that of  $(e_{1g})$ .<sup>†</sup> Hence, the symmetry of the above excited state can be obtained by direct product of  $E_{1g}$  and  $E_{2u}$  which gives

$$E_{1g} \times E_{2u} \rightarrow B_{1u} + B_{2u} + E_{1u}$$

Hence, the transition moment integrals involve the following direct product.

<i>z</i> -components	$A_{1g} \times A_{2u} \times B_{1u} = B_{2g}$	Symmetry
	$A_{1g} \times A_{2u} \times B_{2u} = B_{1g}$	forbidden
	$A_{1g} \times A_{2u} \times E_{1u} = E_{1g}$	transition

*x* and *y* components  $A_{1g} \times E_{1u} \times B_{1u} = E_{2g}$

$$A_{1g} \times E_{1u} \times B_{2u} = E_{2g}$$

$$\begin{aligned} A_{1g} \times E_{1u} \times E_{1u} &= A_{1g} \times (A_{1g} + A_{2g} + E_{2g}) \\ &= A_{1g} \times A_{1g} + A_{1g} \times A_{2g} + A_{1g} \times E_{2g} \\ &= A_{1g} + A_{2g} + E_{2g} \end{aligned}$$

Since  $A_{1g} \times E_{1u} \times E_{1u}$  contains  $A_{1g}$  as one of the representations, the transition  $E_{1u} \leftarrow A_{1g}$  is a symmetry allowed transition.

The spin selection rule states that the spin of electron during electronic transition remains the same, the spin multiplicity of the excited state will remain the same as that of ground state. Since the orbitals in the ground state are fully occupied, the spin multiplicity of the ground state is one. This will be preserved during the transition and hence the electronic spectrum of benzene will include one absorption due to the transition  ${}^1E_{1u} \leftarrow {}^1A_{1g}$ .

<sup>†</sup> In general, if a shell has a total capacity of  $n$  electrons, then the symmetry properties of an electronic configuration containing  $(n - m)$  electrons are exactly identical to that containing  $m$  electrons. This behaviour is explained on the basis that there exists  $m$  holes in a configuration containing  $n - m$  electrons and these holes have the same properties as  $m$  electrons in an empty shell.

<sup>‡</sup> Besides  ${}^1E_{1u}$  state, the other states of the arrangement  $(a_{2u})^2 (e_{1g})^3 (e_{2u})^1$  are  ${}^1B_{2u}$ ,  ${}^3B_{1u}$ ,  ${}^3B_{2u}$  and  ${}^3E_{1u}$ , since the single electron in each of  $e_{1g}$  and  $e_{2u}$  orbitals may have parallel ( $S = 1$ ) and antiparallel ( $S = 0$ ) spins.

## 24 CORRELATION DIAGRAMS FOR A $d^2$ ION IN AN OCTAHEDRAL AND TETRAHEDRAL ENVIRONMENTS

### rm Symbols for Configuration a Free Ion

The number of ways of assigning two electrons ( $N = 2$ ) amongst ten spin orbitals ( $G = 10$ ) involving  $d$  orbitals is given by

$$\frac{G!}{N!(G-N)!} = \frac{10!}{2!8!} = 45 \quad (5.24.1)$$

These forty five configurations along with their  $M_l$  and  $M_s$  values are listed in Table 5.24.1.

The assignment of terms symbols goes as follows.

- The largest value of  $M_l$  is +4. This implies  $L = 4$  and the nine permitted values of  $M_l$  are +4, +3, +2, +1, 0, -1, -2, -3 and -4.

The maximum value of  $M_s$  associated with  $M_l = 4$  is 0. This implies that  $S = 0$ . Thus the spin multiplicity is  $2S + 1 = 2 \times 0 + 1 = 1$ .

There are thus nine configurations for  $L = 4$  and  $S = 0$  state. These may be represented by the configurations, 1, 3, 5, 7, 9, 29, 35, 42 and 45.

The value of  $J = L + S = 4 + 0 = 4$ .

The symbol for  $L = 4$  is G.

Hence, the term symbol for the above nine configurations for  $L = 4$  and  $S = 0$  state is  ${}^1G_4$ .

- In the remaining configurations, the maximum value of  $M_l = 3$ . This implies that  $L = 3$  and the seven permitted values of  $M_l$  are +3, +2, +1, 0, -1, -2 and -3.

Associated with  $M_l = +3$ , the maximum value of  $M_s = +1$ . This implies  $S = 1$  and the permitted values of  $M_s$  are +1, 0 and -1 (i.e. the spin multiplicity is  $2S + 1 = 2 \times 1 + 1 = 3$ ).

Thus, with each of seven values of  $M_l$ , there are three values of  $M_s$ . Hence, there are a total of twenty one configurations associated with  $L = 3$  and  $S = 1$  state. These may be represented by the configurations 2, 10, 11, 4, 18, 13, 19, 20, 26, 21, 22, 28, 23, 24, 30, 34, 38, 39, 41, 43 and 44.

The symbol for  $L = 3$  is F.

Hence, the term symbol for  $L = 3$  and  $S = 1$  is  ${}^3F$ . The permitted values of  $J$  are  $L + S$ ,  $L + S - 1$ , ...,  $|L - S|$ . This gives  $J = 4, 3$  and 2. Thus, the term symbols for  $L = 3$  and  $S = 1$  state are  ${}^3F_4$ ,  ${}^3F_3$  and  ${}^3F_2$ .

- The next maximum value of  $M_l = +2$ . This implies  $L = 2$  and the permitted values of  $M_l$  are +2, +1, 0, -1 and -2.

Table 5.24.1 Forty Five Electronic Configurations for  $d^2$  ion

S.N.	Configuration	$M_l$	$M_s$	S.N.	Configuration	$M_l$	$M_s$	S.N.	Configuration	$M_l$	$M_s$
1	$d_{+2} \bar{d}_{+2}$	+4	0	16	$\bar{d}_{+2} d_{-2}$	0	0	31	$d_0 \bar{d}_0$	0	0
2	$d_{+2} d_{+1}$	+3	1	17	$\bar{d}_{+2} \bar{d}_{-2}$	0	-1	32	$d_0 d_{-1}$	-1	1
3	$d_{+2} \bar{d}_{+1}$	+3	0	18	$d_{+1} \bar{d}_{+1}$	+2	0	33	$d_0 \bar{d}_{-1}$	-1	0
4	$d_{+2} d_0$	+2	1	19	$d_{+1} d_0$	+1	1	34	$d_0 d_{-2}$	-2	1
5	$d_{+2} \bar{d}_0$	+2	0	20	$d_{+1} \bar{d}_0$	+1	0	35	$d_0 \bar{d}_{-2}$	-2	0
6	$d_{+2} d_{-1}$	+1	1	21	$d_{+1} d_{-1}$	0	1	36	$\bar{d}_0 d_{-1}$	-1	0
7	$d_{+2} \bar{d}_{-1}$	+1	0	22	$d_{+1} \bar{d}_{-1}$	0	0	37	$\bar{d}_0 \bar{d}_{-1}$	-1	-1
8	$d_{+2} d_{-2}$	0	1	23	$d_{+1} d_{-2}$	-1	1	38	$\bar{d}_0 d_{-2}$	-2	0
9	$d_{+2} \bar{d}_{-2}$	0	0	24	$d_{+1} \bar{d}_{-2}$	-1	0	39	$\bar{d}_0 \bar{d}_{-2}$	-2	-1
10	$\bar{d}_{+2} d_{+1}$	+3	0	25	$\bar{d}_{+1} d_0$	+1	0	40	$d_{-1} \bar{d}_{-1}$	-2	0
11	$\bar{d}_{+2} \bar{d}_{+1}$	+3	-1	26	$\bar{d}_{+1} \bar{d}_0$	+1	-1	41	$d_{-1} d_{-2}$	-3	1
12	$\bar{d}_{+2} d_0$	+2	0	27	$\bar{d}_{+1} d_{-1}$	0	0	42	$d_{-1} \bar{d}_{-2}$	-3	0
13	$\bar{d}_{+2} \bar{d}_0$	+2	-1	28	$\bar{d}_{+1} \bar{d}_{-1}$	0	-1	43	$\bar{d}_{-1} d_{-2}$	-3	0
14	$\bar{d}_{+2} d_{-1}$	+1	0	29	$\bar{d}_{+1} d_{-2}$	-1	0	44	$\bar{d}_{-1} \bar{d}_{-2}$	-3	-1
15	$\bar{d}_{+2} \bar{d}_{-1}$	+1	-1	30	$\bar{d}_{+1} \bar{d}_{-2}$	-1	-1	45	$d_{-2} \bar{d}_{-2}$	-4	0

The maximum value of  $M_s$  associated with  $M_l = +2$  is 0. The spin multiplicity is  $2S + 1 = 2 \times 0 + 1 = 1$ .

There are thus five configurations for  $L = 2$  and  $S = 0$  state. These may be represented as 12, 14, 16, 36 and 40.

The term symbol of  $L = 2$  is D. The permitted value of  $J$  is  $L + S = 2$ .

Hence, the term symbol for  $L = 2$  and  $S = 0$  state is  ${}^1D_2$ .

- The next maximum value of  $M_l = +1$ . This implies  $L = 1$  and the permitted values of  $M_l$  are +1, 0 and -1.

The maximum value of  $M_s$  associated with  $M_l = +1$  is 1. Thus, the permitted values of  $M_s$  are +1, 0 and -1 (i.e. the spin multiplicity is  $2S + 1 = 2 \times 1 + 1 = 3$ ).

For each of the three values of  $M_l$ , there are three values of  $M_s$ . Hence, there are nine configurations associated with  $L = 1$  and  $S = 1$ . These may be represented by the configurations 6, 25, 15, 8, 27, 17, 32, 33 and 37.

The term symbol for  $L = 1$  is P. The permitted values of  $J$  are  $L + S$ ,  $L + S - 1$ , ...,  $|L - S|$ , i.e. 2, 1 and 0. Hence, the term symbols for  $L = 1$  and  $S = 1$  are  ${}^3P_2$ ,  ${}^3P_1$  and  ${}^3P_0$ .

- The only remaining configuration is 3f for which  $M_L = 0$  and  $M_S = 0$ . This implies  $L = 0$  and  $S = 0$ .

The spin multiplicity is  $2S + 1 = 2 \times 0 + 1 = 1$

The term symbol for  $L = 0$  is S.

The value of  $J = 0$  ( $= L + S$ )

Thus, the term symbol for  $L = 0$  and  $S = 0$  is  ${}^1S_0$ .

- Thus, the term symbols for  $d^2$  configuration are

$${}^1G_4, {}^3F_4, {}^3F_3, {}^3F_2, {}^1D_2, {}^3P_2, {}^3P_1, {}^3P_0 \text{ and } {}^1S_0 \quad (5.24.2)$$

The wave functions of d orbitals may be chosen as the basis for a reducible representation of the point group  $O_h$ . Since the d orbitals are even to inversion, the characters of reducible representation can be obtained by using the pure rotational subgroup O and then adding the subscript 'g' to each of them.

In general, an orbital is represented as

$$\psi = R, \Theta_\theta \Phi_\phi$$

where (i) the function  $R$  is invariant to all operations in a point group,

(ii) the function  $\Theta$  is also invariant if rotation is carried out about the z-axis with respect to which the angle  $\theta$  is measured (since the angle  $\theta$  remains constant during the rotation),

and (iii) the function  $\Phi$  varies since the angle  $\phi$  is varied during the rotation about the z-axis.

Hence, the function  $\Phi$  needs only to be considered to determine the character of reducible representation for the point group O.

Leaving aside the normalization constant, the function  $\Phi$  is given by

$$\Phi = e^{im\phi}$$

For d orbital,  $m = +2, +1, 0, -1$  and  $-2$ .

If a rotation about the z-axis is carried out by an angle  $\alpha$ , its effect on d orbitals is represented as

$$\begin{array}{c|ccccc} e^{2i(\phi+\alpha)} & e^{2i\alpha} & 0 & 0 & 0 & 0 \\ e^{i(\phi+\alpha)} & 0 & e^{i\alpha} & 0 & 0 & 0 \\ e^0 & 0 & 0 & e^0 & 0 & 0 \\ e^{-i(\phi+\alpha)} & 0 & 0 & 0 & e^{-i\alpha} & 0 \\ e^{-2i(\phi+\alpha)} & 0 & 0 & 0 & 0 & e^{-2i\alpha} \end{array}$$

The character of the transformation matrix is

$$\begin{aligned} \chi(\alpha) &= e^{2i\alpha} + e^{i\alpha} + e^0 + e^{-i\alpha} + e^{-2i\alpha} \\ &= \frac{\sin\left(2 + \frac{1}{2}\alpha\right)}{\sin(\alpha/2)}; \quad (\alpha \neq 0) \end{aligned} \quad (5.24.3)^\dagger$$

$$\text{Hence, } \chi(C_2) = \frac{\sin 5\pi/2}{\sin \pi/2} = \frac{1}{1} = 1$$

$$\chi(C_3) = \frac{\sin 5\pi/3}{\sin \pi/3} = \frac{-\sin \pi/3}{\sin \pi/3} = -1$$

$$\text{and } \chi(C_4) = \frac{\sin 5\pi/4}{\sin \pi/4} = \frac{-\sin \pi/4}{\sin \pi/4} = -1$$

Hence, the reducible representation is

O	E	6C <sub>4</sub>	3C <sub>2</sub> (=C <sub>4</sub> <sup>2</sup> )	8C <sub>3</sub>	6C <sub>2</sub>
$\chi(R)$	5	-1	1	-1	1

Using the reduction formula

$$a_i = \frac{1}{h_i} \sum_C n_C \chi(C) \chi_i(C)$$

we get

$$a_e = \frac{1}{24} [1(5)(2) + 6(-1)(0) + 3(1)(2) + 8(-1)(-1) + 6(1)(0)] = 1$$

$$a_{t_2} = \frac{1}{24} [1(5)(3) + 6(-1)(-1) + 3(1)(-1) + 8(-1)(0) + 6(1)(1)] = 1$$

Hence,  $\Gamma = e + t_2$

Since d orbitals are even to inversion, we can add subscript g in the above representations to give

$$\Gamma = e_g + t_{2g} \quad (5.24.4)$$

Thus, d orbitals are no longer degenerate under the influence of octahedral symmetry. These split into a triply degenerate set,  $t_{2g}$ , and a doubly degenerate set,  $e_g$ .

From the character table  $O_h$ , we find that

<sup>†</sup> In general, the sum

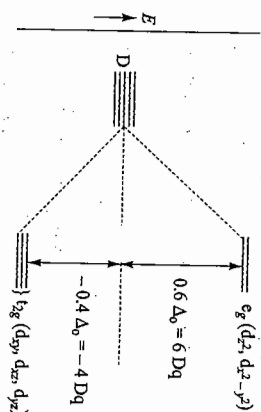
$$e^{i\alpha} + e^{(l-1)\alpha} + \dots + e^{-il\alpha}$$

$$\text{is given by } \chi(\alpha) = \left\{ \sin\left(l + \frac{1}{2}\alpha\right) / \sin(\alpha/2) \right\} \text{ provided } \alpha \neq 0 \quad (5.24.5)$$

## Diagrammatic Representation of Splitting

$e_g$  orbitals are  $d_{2z^2-x^2-y^2}$ ,  $d_{x^2-y^2}$ , i.e.  $d_{z^2}$ ,  $d_{x^2-y^2}$ .  
 $t_{2g}$  orbitals are  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ .

The  $d_{z^2}$  and  $d_{x^2-y^2}$  have lobes along the axes and  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  have lobes midway between the two involved axes, respectively. When a negatively charged ligand approaches the central ion along the axes, it raises the energies of d orbitals along the axes (i.e.  $d_{z^2}$  and  $d_{x^2-y^2}$ ) more than it does for the orbitals lying in between the axes (i.e.  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$ ). Consequently, in the octahedral environments, the energies of d orbitals get affected as shown in Fig. 5.24.1. The splitting is the weighted average such that the total energy of d orbitals in the octahedral environment remains constant.



5.24.1 Effect on energies of d orbitals in octahedral environment

### Configuration of Ion in Large Splitting

In the limit of an extremely large splitting of d orbitals (which occurs when the interactions between central ion and the surrounding ligands are strong), the following configurations may be visualised.

- **Configuration  $t_{2g}^3$**  Both the electrons occupy the stable  $t_{2g}$  orbitals. The direct product of  $t_{2g} \times t_{2g}$  and the irreducible representations contained in it are shown in Table 5.24.2.

Table 5.24.2 Irreducible Representations contained in  $t_{2g}^2$  Configuration

$O_h$	$E$	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	$i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
I $t_{2g}$	3	0	1	-1	-1	3	-1	0	-1	1
II $t_{2g} \times t_{2g}$	9	0	1	1	1	9	1	0	1	1
$A_{1g}$	1	1	1	1	1	1	1	1	1	1
$E_g$	2	-1	0	0	2	2	0	-1	2	0
III $T_{1g}$	3	0	-1	1	-1	3	1	0	-1	-1
$T_{2g}$	3	0	1	-1	-1	3	-1	0	-1	1

The entry I represents irreducible representation  $t_{2g}$ . II represents direct product and III represents irreducible representations in the direct product.

- **Configuration  $t_{2g}^2 e_g$**  Each of the orbitals  $t_{2g}$  and  $e_g$  contains one electron. The direct product  $t_{2g} \times e_g$  and the irreducible representations contained in it are shown in Table 5.24.3.

Table 5.24.3 Irreducible Representations contained in  $t_{2g}e_g$  Configuration

$O_h$	$E$	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	$i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
I $t_{2g}$	3	0	1	-1	-1	3	-1	0	-1	1
$e_g$	2	-1	0	0	2	2	0	-1	2	0
II $t_{2g} \times e_g$	6	0	0	0	-2	6	0	0	-2	0
III $T_{1g}$	3	0	-1	1	-1	3	1	0	-1	-1
$T_{2g}$	3	0	0	-1	-1	3	-1	0	-1	1

The entry I represents the irreducible representations, II represents direct product and III represents the irreducible representations in the direct product.

- **Configuration  $e_g^2$**  Both the electrons are excited to  $e_g$  orbitals. The direct product of  $e_g \times e_g$  and the irreducible representations contained in it are shown in Table 5.24.4.

Table 5.24.4 Irreducible Representations contained in  $e_g^2$  Configuration

$O_h$	$E$	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	$i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
I $e_g$	2	-1	0	0	2	2	0	-1	2	0
II $e_g^2$	4	1	0	0	4	4	0	1	4	0
$A_{1g}$	1	1	1	1	1	1	1	1	1	1
III $A_{2g}$	1	1	-1	-1	1	1	-1	1	1	-1
$E_g$	2	-1	0	0	2	2	0	-1	2	0

The entry I represents the irreducible representation, II represents direct product and III represents the irreducible representations in the direct product.

### Splitting of the Terms of an Ion Under Weak Interactions

The splitting of S, P, D, ... terms of an ion involving more than one electron under the influence of an octahedral environment (or any other environment) follows the same pattern as those of one-electron s, p, d, ... orbitals, respectively. This is based on the fact that both involve the same type of  $\phi$ -dependent function. It is  $\exp(iM\phi)$  for a term and  $\exp(im\phi)$  for an orbital.

The splitting of one-electron d orbitals has been worked out earlier. The same pattern is followed by the term D and thus it splits into  $E_g$  and  $T_{2g}$  representations under the octahedral environment. Following the same procedure, the splitting of other orbitals can be worked out. For s, p, f and g orbitals, splittings are as follows.

Since s orbital has a spherical symmetry with no  $\theta$  and  $\phi$ -dependence terms, the representation based on s orbital will include one as the character in all the rotational operations. Hence, the term S belongs to  $A_{1g}$  representation.

For p orbitals  $l = 1$ . The character of rotational operation as given by Eq. (5.24.5) is

$$\chi(R) = \frac{\sin\left(l + \frac{1}{2}\right)\alpha}{\sin(\alpha/2)} = \frac{\sin(3\alpha/2)}{\sin(\alpha/2)}$$

Hence, we have

$$C_2 \text{ rotation } \alpha = 180^\circ \quad \chi_R = \frac{\sin 270^\circ}{\sin 90^\circ} = -\frac{\sin 90^\circ}{\sin 90^\circ} = -1$$

$$C_3 \text{ rotation } \alpha = 120^\circ \quad \chi_R = \frac{\sin 180^\circ}{\sin 60^\circ} = 0$$

$$C_4 \text{ rotation } \alpha = 90^\circ \quad \chi_R = \frac{\sin 135^\circ}{\sin 45^\circ} = \frac{\sin 45^\circ}{\sin 45^\circ} = 1$$

The reducible representation of which p orbitals form the basis is given by

O	E	$6C_4$	$3C_2 (= C_4^2)$	$8C_3$	$6C_2$
$\chi(R)$	3	1	-1	0	-1

From the character table of the group O, we find that the above representation corresponds to the irreducible representation  $t_1$ . Hence, the term P of  $d^2$  configuration belongs to  $T_{1g}$  representation under octahedral environment.

For f orbitals,  $l = 3$ . The character of rotational operations is given by

$$\chi(R) = \frac{\sin(7\alpha/2)}{\sin(\alpha/2)}$$

Hence, we have

$$C_2 \text{ rotation } \alpha = 180^\circ \quad \chi_R = \frac{\sin 630^\circ}{\sin 90^\circ} = -\frac{\sin 90^\circ}{\sin 90^\circ} = -1$$

$$C_3 \text{ rotation } \alpha = 120^\circ \quad \chi_R = \frac{\sin 420^\circ}{\sin 60^\circ} = \frac{\sin 60^\circ}{\sin 60^\circ} = 1$$

$$C_4 \text{ rotation } \alpha = 90^\circ \quad \chi_R = \frac{\sin 315^\circ}{\sin 45^\circ} = -\frac{\sin 45^\circ}{\sin 45^\circ} = -1$$

The reducible representation for which f orbitals form the basis is

O	E	$6C_4$	$3C_2 (= C_4^2)$	$8C_3$	$6C_2$
$\chi(R)$	7	-1	-1	1	-1

From the character table of the group O, this is equivalent to  $a_2 + t_1 + t_2$ . Since orbitals are odd to inversion, the f orbitals split into  $a_{2g}$ ,  $t_{1u}$  and  $t_{2u}$ .

The term F under octahedral symmetry will split into  $A_{2g}$ ,  $T_{1g}$  and  $T_{2g}$ .

For g orbitals,  $l = 4$ . The character of rotational operation is given by

$$\chi(R) = \frac{\sin(9\alpha/2)}{\sin(\alpha/2)}$$

Hence, we have

$$C_2 \text{ rotation } \alpha = 180^\circ \quad \chi(R) = \frac{\sin 810^\circ}{\sin 90^\circ} = \frac{\sin 90^\circ}{\sin 90^\circ} = 1$$

$$C_3 \text{ rotation } \alpha = 120^\circ \quad \chi(R) = \frac{\sin 540^\circ}{\sin 60^\circ} = \frac{\sin 180^\circ}{\sin 60^\circ} = 0$$

$$C_4 \text{ rotation } \alpha = 90^\circ \quad \chi(R) = \frac{\sin 405^\circ}{\sin 45^\circ} = \frac{\sin 45^\circ}{\sin 45^\circ} = 1$$

The reducible representation for which g orbitals form the basis is

O	E	$6C_4$	$3C_2 (= C_4^2)$	$8C_3$	$6C_2$
$\chi(R)$	9	1	1	0	1

From the character table of the group O, this is equivalent to  $a_1$ ,  $e$ ,  $t_1$  and  $t_2$ . Since g orbitals are even to inversion, the g orbitals split into  $a_{1g}$ ,  $e_g$ ,  $t_{1g}$  and  $t_{2g}$ .

The term G splits into  $A_{1g}$ ,  $E_g$ ,  $T_{1g}$  and  $T_{2g}$  representations in an octahedral environment.

The chemical environment does not interact directly with the electron spins and thus the states splitted from a particular term have the same spin multiplicity as that of the involved terms. Table 5.24.5 correlates terms with states along with spin multiplicity and their numbers.

**Table 5.24.5 Correlation between Terms and the Corresponding States**

Term	No. of configurations $S(2L+1)$	States	No. of states <sup>†</sup> $\Sigma a \times b$
$^1S$	$(1)(2 \times 0 + 1) = 1$	$^1A_{1g}$	$1 \times 1 = 1$
$^3P$	$(3)(2 \times 1 + 1) = 9$	$^3T_{1g}$	$3 \times 3 = 9$
$^1D$	$(1)(2 \times 2 + 1) = 5$	$^1E_g$ and $^1T_{2g}$	$1 \times 2 + 1 \times 3 = 5$
$^3F$	$(3)(2 \times 3 + 1) = 21$	$^3A_{2g}$ , $^3T_{1g}$ and $^3T_{2g}$	$3 \times 1 + 3 \times 3 + 3 \times 3 = 21$
$^1G$	$(1)(2 \times 4 + 1) = 9$	$^1A_{1g}$ , $^1E_g$ , $^1T_{1g}$ and $^1T_{2g}$	$1 \times 1 + 1 \times 2 + 1 \times 3 + 1 \times 3 = 9$

<sup>†</sup>  $a \times b$  involves spin-multiplicity  $a$  and dimension  $b$  of the state.

### Construction of Correlation Diagram

The correlation diagram for a  $d^2$  ion in an octahedral environment may be drawn as described in the following.

- On the extreme left, the free-ion terms (Eq. 5.24.2) in the increasing order of energies are depicted. Experimentally, it is found that

$$E(^3F) < E(^1D) < E(^3P) < E(^1G) < E(^1S)$$

Immediately right to the above energies, the states into which these free-ion terms split under the influence of weak interaction in the octahedral environment are depicted. The spin multiplicities of these states are the same as that of the corresponding free-ion terms.

- On the, extreme right, the energy levels of the three configurations  $t_{2g}^2 e_g$  and  $e_g^2$  in the increasing order are depicted. The energy difference between the two successive levels is  $\Delta_0$ . These are configurations which one observes in the limit of an extremely large splitting of the d orbitals which occurs in the presence of strong interaction between the ion and the octahedral environment. Immediately left to these levels, the states involved in these levels are shown which arise due to the relaxation of strong interaction between the ion and the environment. However, the spin multiplicity of these states are not known as the distribution of two electrons may lead to singlets or triplets.

- In constructing the correlation diagram, the following two principles hold good.
  1. In going from weak to strong interactions with the environment, the symmetry properties as well as their spin multiplicity are preserved. Thus, there must exit a one-to-one correspondence between the states on the either sides of the correlation diagram.
  2. In going from weak to strong interactions with the environment, the states of the same spin multiplicity and symmetry do not cross each other. This is known as non-crossing rule.

Guided by these principles, we can correlate states on either sides as described in the following.

- There is only one  $A_{2g}$  state on either side of the diagram— $^3A_{2g}$  in the term  $^3F$  and  $A_{2g}$  in the energy level  $e_g^2$ . We join these two states. Since the spin multiplicity is preserved, the  $A_{2g}$  state in  $e_g^2$  level must also be triplet.
- There are two  $A_{1g}$  states on either side of the diagram— $^1A_{1g}$  in  $^1S_1$  and  $^1A_{1g}$  in  $^1G$ , and  $A_{1g}$  in  $e_g^2$  and  $A_{1g}$  in  $t_{2g}^2$ . In accordance with the non-crossing rule, we join  $^1A_{1g}$  of  $^1S_1$  with  $A_{1g}$  of  $e_g^2$  and  $^1A_{1g}$  of  $^1G$  with  $A_{1g}$  of  $t_{2g}^2$ . This also establishes that  $A_{1g}$  in each of  $e_g^2$  and  $t_{2g}^2$  is singlet.
- There are two  $E_g$  states on either side of the diagram— $^1E_g$  in  $^1G$  and  $^1E_g$  in  $^1D$ , and  $E_g$  in  $e_g^2$  and  $E_g$  in  $t_{2g}^2$ . In accordance with the non-crossing rule, we join  $^1E_g$  of  $^1G$  with  $E_g$  of  $e_g^2$  and  $^1E_g$  of  $^1D$  with  $E_g$  of  $t_{2g}^2$ . This also establishes that  $E_g$  in each of  $e_g^2$  and  $t_{2g}^2$  is singlet.
- We are left with three  $T_{1g}$  and three  $T_{2g}$  states. On left side, we have  $^3T_{1g}$ ,  $^3T_{2g}$ , and  $^1T_{1g}$ ,  $^1T_{2g}$ . Since on right side, there are two  $T_{1g}$  and two  $T_{2g}$  states in  $t_{2g}e_g$ , we propose that each of the two involves one singlet and one triplet, i.e.  $^1T_{1g}$ ,  $^3T_{1g}$  and  $^1T_{2g}$ ,  $^3T_{2g}$ . We are left with one  $^3T_{1g}$  and  $^1T_{2g}$  on the left side, we associate these states to the  $t_{2g}^2$  level.
- We join single  $^3T_{2g}$  in  $^3F$  with  $^3T_{2g}$  of  $t_{2g}e_g$  and single  $^1T_{1g}$  in  $^1G$  with  $^1T_{1g}$  of  $t_{2g}e_g$ .

- In accordance with the non-crossing rule, we join  $^3T_{1g}$  of  $^3F$  with  $^3T_{1g}$  of  $t_{2g}^2$  and  $^3T_{1g}$  of  $^3F$  with  $^3T_{1g}$  of  $t_{2g}e_g$ . For the same reason, we join  $^1T_{2g}$  of  $^1D$  with  $^1T_{2g}$  of  $t_{2g}^2$  and  $^1T_{2g}$  of  $^1D$  with  $^1T_{2g}$  of  $t_{2g}e_g$ .

This completes the correlation diagram and is shown in Fig. 5.24.2. This diagram is known as Tanabe and Sugano diagram. While interpreting electronic spectra, Orgel diagram is more useful as it depicts only those terms that have the same multiplicity as the ground state.

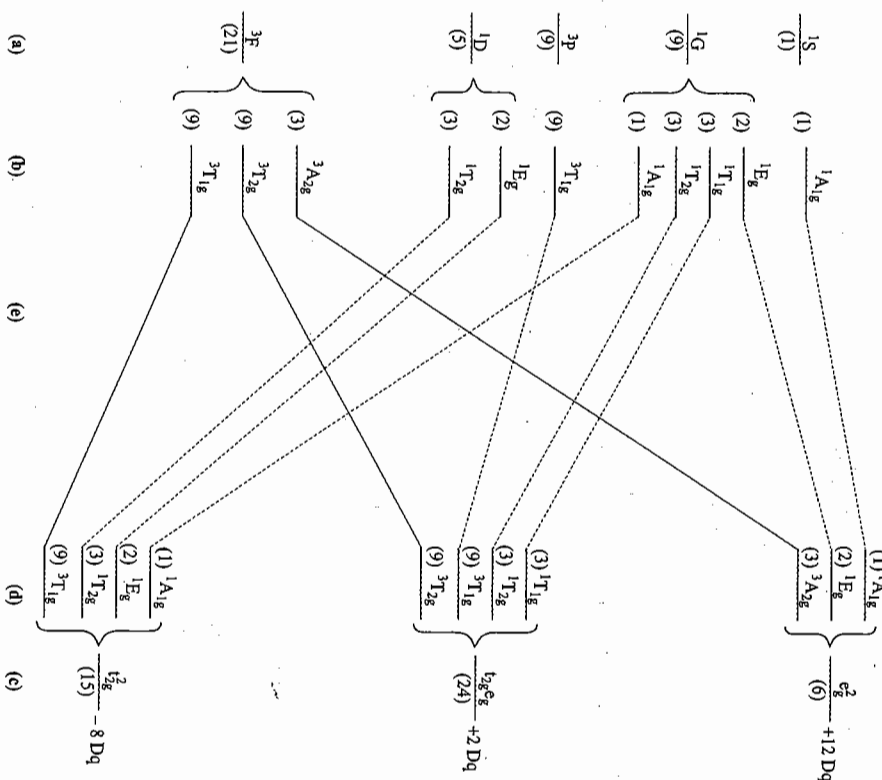


Fig. 5.24.2 Correlation diagram of  $d^2$  ion in octahedral environment. The total degeneracy of each level is given in parentheses. (a) Spherically perturbed free ion spectroscopic terms. (b) Group theoretical terms in a weak octahedral field. (c) Electronic configurations in a strong octahedral field, inclusive of interelectronic repulsion. (d) Group theoretical terms in a strong octahedral field, inclusive of interelectronic repulsion. (e) Intermediate field region

### The Method of Descending Symmetry

The spin multiplicity of the states arising from the energy levels  $t_{2g}$  and  $e_g^2$  when the strong interactions of the ion with the environment is relaxed can be ascertained by the method of descending symmetry. This method is based on the principle that the spin multiplicity of a state is not changed on descending the symmetry.

**States arising from the  $t_{2g}^2$  configuration** The level  $t_{2g}^2$  leads to  $A_{1g}$ ,  $E_g$ ,  $T_{1g}$  and  $T_{2g}$  representations. We look the transformation table\* where each of the above representations in the group  $O_h$  are changed or decomposed into one-dimensional representation or sum of one-dimensional representations in its subgroup of lower symmetry. The subgroup satisfying this condition is  $C_{2h}$  or  $C_{2v}$ .

Selecting the subgroup  $C_{2h}$  we find the following transformations

$O_h$	$C_{2h}$
$A_{1g}$	$A_g$
$E_g$	$A_g + B_g$
$T_{1g}$	$A_g + B_g + B_g$
$T_{2g}$	$A_g + A_g + B_g$

Since  $t_{2g}$  in  $O_h$  goes over to  $a_g + a_g + b_g$  in  $C_{2h}$ . We write two  $a_g$  as  $a_g(1)$  and  $a_g(2)$ . The direct product  $t_{2g} \times t_{2g}$  goes into sum of the six direct products listed below.

$$a_g(1) \times a_g(1) = A_g$$

$$a_g(1) \times a_g(2) = A_g \text{ and } A_g$$

$$a_g(1) \times b_g = B_g \text{ and } B_g$$

$$a_g(2) \times a_g(2) = A_g$$

$$a_g(2) \times b_g = B_g \text{ and } B_g$$

$$b_g \times b_g = A_g$$

Both the electrons belong to the same orbital  $a_g(1)$ .

Each of the two electrons belongs to different orbitals

Each of the two electrons belongs to different orbitals  $a_g(1)$  and  $b_g$

Both the electrons belong to the same orbital  $a_g(2)$

Each of the two electrons belongs to different orbitals  $a_g(2)$  and  $b_g$

Both the electrons belong to the same orbital  $b_g$

\* The transformation table is as follows.

$O_h$	$T_d$	$D_{4h}$	$D_{2d}$	$D_2$	$C_{4v}$	$C_{2h}$	$C_{2v}$
$A_{1g}$	$A_1$	$A_{1g}$	$A_1$	$A_1$	$A_1$	$A_g$	$A_1$
$A_{2g}$	$A_2$	$B_{1g}$	$B_1$	$A_2$	$B_1$	$B_g$	$A_2$
$E_g$	$E$	$A_{1g} + B_{1g}$	$A_1 + B_1$	$E$	$A_1 + B_1$	$A_g + B_g$	$A_1 + A_2$
$T_{1g}$	$T_1$	$A_{2g} + E_g$	$A_2 + E$	$A_2 + E$	$A_2 + E$	$A_g + 2B_g$	$A_2 + B_1 + B_2$
$T_{2g}$	$T_2$	$B_{2g} + E_g$	$B_2 + E$	$A_1 + E$	$B_2 + E$	$2A_g + B_g$	$A_1 + B_1 + B_2$
$A_{1u}$	$A_2$	$B_{1u}$	$B_1$	$A_1$	$A_2$	$A_u$	$A_2$
$A_{2u}$	$A_1$	$B_{1u}$	$B_1$	$A_2$	$B_2$	$B_u$	$A_1$
$E_u$	$E$	$A_{1u} + B_{1u}$	$A_1 + B_1$	$E$	$A_2 + B_2$	$A_u + B_u$	$A_1 + A_2$
$T_{1u}$	$T_2$	$A_{2u} + E_u$	$B_2 + E$	$A_2 + E$	$A_1 + E$	$A_u + 2B_u$	$A_1 + B_1 + B_2$
$T_{2u}$	$T_1$	$B_{2u} + E_u$	$A_2 + E$	$A_1 + E$	$B_1 + E$	$2A_u + B_u$	$A_2 + B_1 + B_2$

Hence  $T_{2g}^2$  leads to  $4^1A_g + 3^1A_g + 2^1B_g + 2^3B_g$ , a total of nine representations. With degeneracy equal to 15 [ $= 4(1 \times 1) + 1(3 \times 1) + 2(1 \times 1) + 2(3 \times 1)$ ].

Since there is only one  $3^1A_g$  state and two  $3^3B_g$  states, and these are the states obtained from  $T_{1g}$  on descending from  $O_h$  to  $C_{2h}$ , we assign triple spin-multiplicity to the state  $T_{1g}$ . All remaining states are singlet and can be assigned without any ambiguity. Hence, the designation of spin-multiplicity goes as follows.

$O_h$	$C_{2h}$
$1^1A_{1g}$	$1^1A_g$
$1^1E_g$	$1^1A_g + 1^1B_g$
$3^1T_{1g}$	$3^1A_g + 3^1B_g + 3^1B_g$
$1^1T_{2g}$	$1^1A_g + 1^1B_g$

**States arising from  $e_g^2$  configuration** The level  $e_g^2$  leads to  $A_{1g}$ ,  $A_{2g}$  and  $E_g$  representations. On lowering the symmetry to  $D_{4h}$ , we find the following transformations.

$O_h$	$D_{4h}$
$A_{1g}$	$A_{1g}$
$A_{2g}$	$B_{1g}$
$E_g$	$A_{1g} + B_{1g}$

Since  $e_g$  in  $O_h$  goes over to  $a_{1g} + b_{1g}$  in  $D_{4h}$ , the direct product  $e_g^2$  goes into sum of the three direct products listed below.

$$a_{1g} \times a_{1g} = A_{1g}$$

$$a_{1g} \times b_{1g} = B_{1g} \text{ and } B_{1g}$$

$$b_{1g} \times b_{1g} = A_{1g}$$

Both the electrons belong to the same orbital  $a_{1g}$

Each of the two electrons belongs to different orbitals

Both the electrons belong to the same orbital  $b_{1g}$

Hence,  $e_g^2$  leads to  $2^1A_{1g} + 1^1B_{1g} + 3^1B_{1g}$ , a total of four representations with degeneracy equal to six [ $= 2(1 \times 1) + 1(1 \times 1) + 1(3 \times 1) = 6$ ].

Since there is only one  $3^1B_{1g}$  state and this state is obtained from  $A_{2g}$  on descending from  $O_h$  to  $D_{4h}$ , we assign triple spin-multiplicity to the state  $A_{2g}$ . All remaining states are single and can be assigned without any ambiguity. Hence, the designation of spin-multiplicity goes as follows.

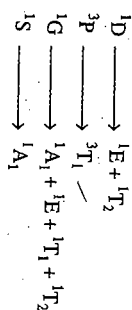
$O_h$	$D_{4h}$
$1^1A_{1g}$	$1^1A_{1g}$
$3^1A_{2g}$	$3^1B_{1g}$
$1^1E_g$	$1^1A_{1g} + 1^1B_{1g}$

### CORRELATION DIAGRAM FOR A $d^2$ ION IN A TETRAHEDRAL ENVIRONMENT

Following the procedure for the octahedral environment, the correlation diagram for a  $d^2$  ion in a tetrahedral environment can be constructed.

The terms for  $d^2$  configuration under the tetrahedral environment split as follows.

$$3F \longrightarrow 3A_2 + 3T_1 + 3T_2$$



Under the influence of tetrahedral symmetry, d orbitals are no longer degenerate. They split into a doubly degenerate set  $e$  and a triple degenerate set  $t$  as shown in Fig. 5.24.3.

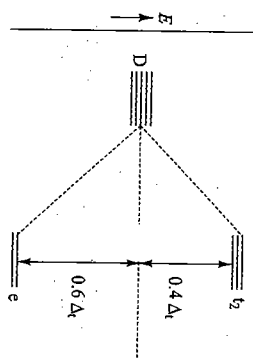
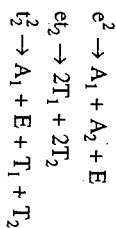


Fig. 5.24.3 Effect of energies of d orbitals in tetrahedral symmetry

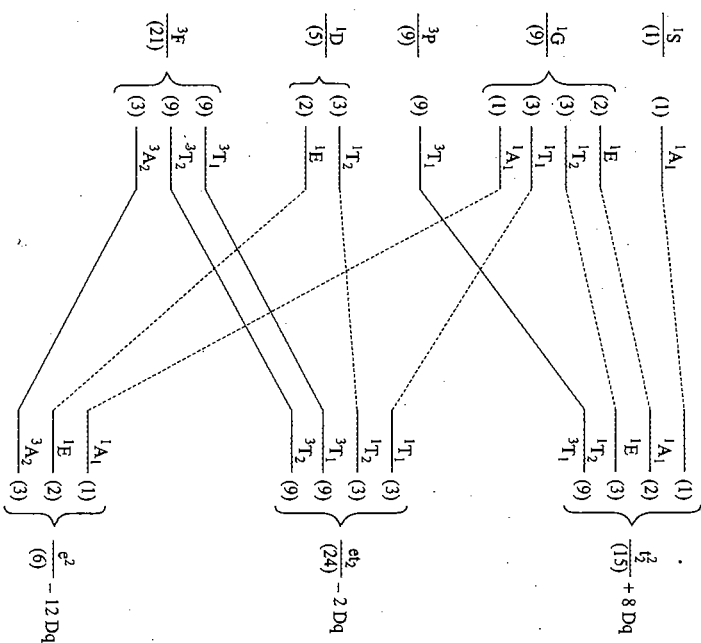
The three electronic configurations under the influence of a strong interaction with the tetrahedral environment in the increasing order of energy are  $e^2$ ,  $e_t$  and  $t_2^2$ . The direct product of each of these configurations yields the following constituent irreducible representations:



The correlation (Fig. 5.24.4) diagram can be completed by joining the states on left side (weak interaction) with those of right side (strong interaction) as described in the following.

- ${}^3A_2$  state in  ${}^3F$  is joined with  $A_2$  state in  $e^2$ , this also establishes the triple spin multiplicity for  $A_2$  state in  $e^2$ .
  - ${}^1A_1$  state in  ${}^1S$  is joined with  $A_1$  state in  $t_2^2$  and  ${}^1A_1$  in  ${}^1G$  is joined with  $A_1$  state in  $e^2$ . These also generate single spin multiplicity in both  $A_1$  states on the right side.
  - $E$  state in  ${}^1G$  is joined with  $E$  state in  $t_2^2$  and  $E$  state in  ${}^1D$  is joined with  $E$  state in  $e^2$ , again generating single spin multiplicity in both  $E$  state on the right side.
  - Assigning  $T_1$  states in  $e_t$  as  ${}^1T_1$  and  ${}^3T_1$ , we join the states  ${}^1T_1$  in  $e_t$  with  ${}^1T_1$  in  ${}^1G$  and  ${}^3T_1$  in  $e_t$  with  ${}^3T_1$  in  ${}^3F$ . Similarly assigning  $T_2$  states in  $e_t$  as  ${}^1T_2$  and  ${}^3T_2$ , we join the states  ${}^1T_2$  in  $e_t$  with  ${}^1T_2$  in  ${}^1D$  and  ${}^3T_2$  in  $e_t$  with  ${}^3T_2$  in  ${}^3F$ .
  - We are left with  ${}^3T_1$  in  $P$  and  ${}^1T_2$  in  ${}^1G$  on the left side and  $T_1$  and  $T_2$  in  $t_2^2$  on the right side. Thus, we join  ${}^3T_1$  in  $P$  with  $T_1$  in  $t_2^2$  (establishing triple spin degeneracy in  $T_1$ ) and  ${}^1T_2$  in  ${}^1G$  with  $T_2$  in  $t_2^2$  (establishing triple spin degeneracy in  $T_2$ ).
- This completes the correlation diagram (Fig. 5.24.4).

Fig. 5.24.4 Correlation diagram of  $d^2$  ion in tetrahedral environment



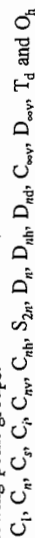
## EXERCISES

- Distinguish between the terms symmetry element and symmetry operation.
- Explain with suitable examples the following symmetry elements and the associated symmetry operations: (a) Axis of rotation, (b) Symmetry planes, (c) Centre of inversion, (d) Improper axis of rotation.
- (a) Describe the sequence of operations in  $S_2$  and  $S_6$  symmetry elements.  
(b) Show that the presence of  $S_n$  with  $n = \text{odd}$  implies the existence of  $C_n$  and  $\sigma$  perpendicular to  $C_n$ .  
(c) Show that the presence of  $S_n$  with  $n = \text{even}$  implies the existence of  $C_{n/2}$  and centre of inversion.  
(d) Show that  $S_4$  with  $n = \text{odd}$  generates  $2n$  operations.
- If there is  $C_2$  axis perpendicular to the principal axis  $C_3$ , show that there will be three such  $C_2$  axis.
- Distinguish amongst the symmetry elements  $C_n$ ,  $\sigma_h$  and  $\sigma_v$ .  
(a) Show that the rotation by  $180^\circ$  followed by reflection in a plane perpendicular to this axis is equivalent to the centre of inversion.  
(b) Using a cube, show geometrically that rotation of  $180^\circ$  successively about  $z$ ,  $y$  and  $x$  axes is equivalent to an identity operation.
- Show geometrically by taking a point in three-dimensional space, the following facts.



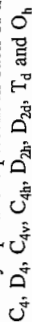
- (i) If there are two  $C_2$  axes perpendicular to each other, there must be a third  $C_2$  axis perpendicular to both
- (ii) If there is a  $C_4$  axis and a plane containing this, there must also be a plane containing  $C_4$  axis at an angle  $45^\circ$  to the first one.
- (iii) If there are  $C_{4(2)}$  and  $C_{2(2)}$  axes, a  $C_2$  axis lying in the 1st and 3rd quadrants of the  $xy$  plane at an angle  $45^\circ$  to  $C_{2(y)}$  must exist.
- (iv) The product of two reflections in planes A and B intersecting at an angle  $\phi$  is equivalent to a rotation by an angle  $2\phi$  about the axis defined by the line intersection of the two planes.

7. (a) What is a point group? Describe the main symmetry elements present in each of the following point groups.



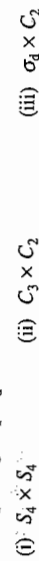
- (b) A molecule contains a  $C_3$  axis and a  $\sigma_h$ . Assign the point group to this molecule. Write down all the symmetry operations and indicate which could be grouped to the same class.

8. List the symmetry operations present in each of the following point groups.

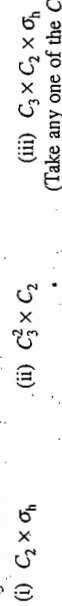


9. (a) Classify the following molecules in the appropriate point groups.  
 $H_2O$ ,  $NH_3$ ,  $CH_4$ ,  $BeH_2$ ,  $BCl_3$ , staggered ethane, allene,  $H_3BO_3$ ,  $PCl_5$ ,  
 naphthalene,  $Cl_2FSO$ ,  $NO_3^-$ ,  $PF_5$ ,  $CO$ ,  $CO_2$ ,  $C_3H_5$ ,  $B_2H_6$ ,  $SF_6$
- (b) In  $NiBr_4^{2-}$  ( $T_d$ ), if one Ni—Br is stretched relative to other without bending, what are the symmetry elements lost and what is the point group? If two of Ni—Br are stretched what is the answer?

10. (a) Indicate which operation is equivalent to the following products of the operations of the point group  $T_d$ .



- (b) Indicate which operator is equivalent to the following products of operations in  $PF_5$  molecule.



11. Describe the scheme for the systematic classification of molecules into various point groups.

12. Explain the term Abelian group.

13. Mention the four characteristics satisfied by a point group. Show that the numbers 1,  $-1$ ,  $i$  and  $-i$  with ordinary multiplication form a group.

14. Show that the reciprocal of a combination of two (or more) elements of a group is equal to the combination of the reciprocals in the reverse order.

15. Construct the group multiplication table for the point group  $C_{3v}$ .

16. (a) Explain the term classes in a point group. How many classes are present in the point group  $C_{3v}$ ?

- (b) A molecule contains a  $C_n$  axis. Do the symmetry operations  $C_n^m$  and  $C_n^{n-m}$  belong to the same class. Another molecule has  $C_n$  axis and a  $C_2$  axis perpendicular to  $C_n$  axis. How many more  $C_2$  axes perpendicular to  $C_n$  are present? Will the symmetry operations around these  $C_2$  axes belong to the same class?

17. Construct the group multiplication table for the point group  $C_{3v}$
18. Taking an example of  $H_2O$  molecule, set up one-dimensional representations of the point group  $C_{2v}$  based on the translational vectors  $T_x$ ,  $T_y$  and  $T_z$
19. Taking an example of  $H_2O$  molecule, set up one-dimensional representations of the point group  $C_{2v}$  based on the rotational vectors  $R_x$ ,  $R_y$  and  $R_z$
20. Taking an example of  $NH_3$  molecule, set up one-dimensional representation of the point group  $C_{3v}$  based on the translational vector  $T_z$  attached to the nitrogen atom.

21. Taking an example of  $NH_3$  molecule, set up two-dimensional representations of the point group  $C_{3v}$  based on the translational vectors  $T_x$  and  $T_y$  attached to the nitrogen atom.

22. Taking an example of  $NH_3$ , set up one-dimensional representation of the point group  $C_{3v}$  based on rotational vectors  $R_z$  attached to the three hydrogen atoms.

23. Set up a two-dimensional representation of the point group  $C_{2v}$  based on the bond vectors associated with the two O—H bonds of water molecule.

24. Set up a three-dimensional representation of the point group  $C_{3v}$  based on the bond vectors associated with the three N—H bonds of  $NH_3$  molecule.

25. Based on  $p_x$ ,  $p_y$  and  $p_z$  orbitals of oxygen atom in  $H_2O$  molecule, set up the one-dimensional representations of the point group  $C_{2v}$ .

26. Based on the five d orbitals of sulphur atom in  $H_2S$  molecule, set up the one-dimensional representations of the point group  $C_{2v}$ .

Set up the one-dimensional representations of s, p and d orbitals in the group  $D_{2h}$ .

Ans.	E	$C_{2x}$	$C_{2y}$	$C_{2z}$	i	$\sigma_{xy}$	$\sigma_{xz}$	$\sigma_{yz}$
$d_{x^2-y^2}, d_{z^2}, s$	1	1	1	1	1	1	1	1
$d_{xy}$	1	1	-1	-1	1	1	-1	-1
$d_{xz}$	1	-1	1	-1	1	-1	1	-1
$d_{yz}$	1	-1	-1	1	1	-1	-1	1
$p_x$	1	-1	-1	1	-1	1	1	-1
$p_y$	1	-1	1	-1	-1	1	-1	1
$p_z$	1	1	-1	-1	-1	-1	1	1

27. Explain the terms 'reducible and irreducible representations'.

28. How is the character of a matrix defined? Show that:

(i) If  $C = AB$  and  $D = BA$ , then the characters of matrices C and D are identical.

(ii) Conjugate matrices have identical characters.

29. State 'The Great Orthogonality Theorem'.

30. (a) Explain the following characteristics followed by irreducible representations of a group.

(i) The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group.

(ii) The sum of the squares of the characters of symmetry operations in any irreducible representations is equal to  $h$ .

(iii) The sum of products of corresponding vectors of two different irreducible representations is equal to zero.

- (iv) In a given representation (reducible or irreducible) the characters of all matrices belonging to the symmetry operations in the same class are identical.
- (b) Show that the characters of the group  $C_{4v}$  obey the orthogonality rules.
- (c) Determine irreducible representations contained in the direct product of the following irreducible representations.
- $A_1 \times A_1$ ;  $A_1 \times A_2$  for  $C_{3v}$
  - $E' \times E'$ ;  $A_1'' \times A_2''$  for  $D_{3h}$
31. Based on the characteristics of irreducible representation, set up the irreducible representations of the point groups  $C_{2v}$  and  $C_{3v}$ .
32. (a) Derive the expression for determining the number of times the  $i$ th irreducible representation present in a reducible representation, i.e. derive the expression
- $$a_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R)$$
- (b) Given are the characters of reducible representations for the indicated groups for the various classes in the order. Determine irreducible representations.
- $C_{2v}$ : 4, -2, 0, -2
  - $C_{3h}$ : 4, 1, 1, 2, -1, -1
  - $O_h$ : 15, 0, -1, 1, 1, -3, 0, 5, -1, 3
33. Set up the reducible representation based on the three translational vectors attached to each atom in  $H_2O$  molecule and resolve it into the irreducible representations.
34. Set up the reducible representation based on the three translational vectors attached to each atom of  $CH_4$  molecule and resolve it into irreducible representations.
35. Set up the reducible representation based on the three translational vectors attached to each atom of *trans*- $N_2F_2$  and resolve it into irreducible representations.
36. (a) Explain the following general layout of a character table

I	II	
III	IV	V
		VI

- (b) Determine from character tables, the representations to which s, p and d orbitals of an atom in a molecule belonging to (i)  $O_h$ , (ii)  $T_d$ , (iii)  $D_{4h}$ , (iv)  $D_3$  groups, (v)  $C_{2v}$ , and (vi)  $C_{3v}$  groups.
37. Describe the Mulliken symbols used to designate irreducible representations.
38. (a) In the group  $D_{3h}$  show that the orbitals
- s and  $d_{z^2}$  belong to  $a_{1g}$ ;  $d_{x^2-y^2}$  belongs to  $b_{1g}$
- $d_{xy}$  belong to  $b_{2g}$ ;  $p_z$  belong to  $a_{2u}$
- and  $d_{xz}$ ,  $d_{yz}$  belong to  $e_g$ ;  $p_x$ ,  $p_y$  belong to  $e_u$
- (Hint: Work out the symmetries using the operations of the group  $D_4$  and then add the subscript g and u as the case may be.)
- (b) In the group  $D_{4h}$  show that the orbitals
- s and  $d_{z^2}$  belong to  $a_1'$ ;  $p_z$  belongs to  $a_2''$
- $p_x$ ,  $p_y$  belong to  $e'$ ;  $d_{xz}$ ,  $d_{yz}$  belong to  $e''$
- and  $d_{x^2-y^2}$  belongs to  $e'$
39. Set up the projection operator  $\hat{P}_i = \frac{1}{h} \sum_R \chi_i(R) \hat{R}$

40. Using the projection operator on the function  $x + y + z$ , show that for the point group  $C_{3v}$  (i)  $z$  forms the basis for  $A_1$  representation, and (ii)  $x$  and  $y$  together form the bases of  $E$  representation
41. Work out the SALC's of  $H_2O$  molecule involving 1s orbitals of hydrogen atoms and also form molecular orbitals of  $H_2O$  molecule.
42. Work out the SALC's of  $BeH_2$  molecule involving 1s orbitals of hydrogen atoms and also form molecular orbitals of  $BeH_2$  molecule.
43. Work out the SALC's of  $BH_3$  molecule involving 1s orbitals of hydrogen atoms and also form molecular orbitals of  $BH_3$  molecule.
44. Work out the SALC's of  $NH_3$  molecule involving 1s orbitals of hydrogen atoms and also form molecular orbitals of  $NH_3$  molecule.
45. Work out the localized and nonlocalized molecular orbitals of  $CH_4$  molecule.
46. Work out SALC's and  $\pi$ -molecular orbitals of *trans*-butadiene.
47. Work out SALC's and  $\pi$ -molecular orbitals of naphthalene.
48. Set up the character tables for the cyclic group of order from two to six involving the element  $E_n = \exp(2\pi i/n)$ .

[Hint: For  $C_6$ , use  $\varepsilon^2 = -\varepsilon^*$  and  $\varepsilon^{2*} = -\varepsilon$ ]

49. (a) Work out the molecular orbitals of allyl radical ( $H_2C=CH-\dot{C}H_2$ , point group  $C_{2v}$ ). Find out their energies and compare with those of cyclopropenyl.

$$\begin{aligned} [\text{Ans: } \psi_1(A_2) &= (1/\sqrt{2})(\phi_1 - \phi_3), E_1 = \alpha \\ \psi_2(B_2) &= (1/2)(\phi_1 + \sqrt{2}\phi_2 + \phi_3); E_2 = \alpha + \sqrt{2}\beta \\ \psi_3(B_2) &= (1/2)(\phi_1 - \sqrt{2}\phi_2 + \phi_3); E_3 = \alpha - \sqrt{2}\beta] \end{aligned}$$

- (b) Work out  $\pi$ -molecular orbitals of cyclopropenyl and their energies.

$$\begin{aligned} [\text{Ans: } \psi_1(A) &= (1/\sqrt{3})(\phi_1 + \phi_2 + \phi_3); E_1 = \alpha \\ \psi_2(E) &= (1/\sqrt{6})(2\phi_1 - \phi_2 - \phi_3); E_2 = \alpha - \beta \\ \psi_3(E) &= (1/\sqrt{2})(\phi_2 - \phi_3); E_3 = \alpha - \beta] \end{aligned}$$

- (c) Work out  $\pi$ -molecular orbitals of benzene.

50. Work out the hybrid orbitals of atom A in the molecule  $AB_3$ .
51. Work out the hybrid orbitals of atom C in the molecule  $CH_4$ .
52. Work out the hybrid orbitals of atom A in a planar molecule  $AB_3$ .
53. Discuss the hybrid orbitals in  $\pi$  bonding in the planar  $AB_3$  and  $AB_4$  molecules.
54. Using SALC's of butadiene, calculate the energies of its molecular orbitals. Also work out its molecular orbitals.
55. Using SALC's of naphthalene, calculate the energies of its molecular orbitals. Also work out its molecular orbitals.
56. Work out the molecular orbitals of tetracyclobutane. Determine its delocalization energy, charge densities and bond orders.
57. Work out the molecular orbitals of trivinylmethyl radical.

# ANNEXURE Some Commonly Used Character Tables

## 1. The $C_n$ Groups

$C_2$	E	$C_2$		
A	1	1	$z, R_z$	$x^2, y^2, z^2, xy$
B	1	-1	$x, y, R_x, R_y$	$yz, xz$

$C_3$	E	$C_3$	$C_3^2$	$\varepsilon = \exp(2\pi i/3)$	
A	1	1	1	$z, R_z$	$x^2 + y^2, z^2$
E	$\begin{Bmatrix} 1 & \varepsilon \\ 1 & \varepsilon^* \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon & \varepsilon^* \\ \varepsilon^* & \varepsilon \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^2 & \varepsilon \\ \varepsilon & \varepsilon^2 \end{Bmatrix}$	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (yz, xz)$

$C_4$	E	$C_4$	$C_2$	$C_4^3$		
A	1	1	1	1	$z, R_z$	$x^2 + y^2, z^2$
B	1	-1	1	-1		$x^2 - y^2, xy$
E	$\begin{Bmatrix} 1 & i \\ 1 & -i \end{Bmatrix}$	$\begin{Bmatrix} i & -1 \\ -1 & -i \end{Bmatrix}$	$\begin{Bmatrix} -1 & i \\ i & 1 \end{Bmatrix}$	$\begin{Bmatrix} -i & -1 \\ -1 & i \end{Bmatrix}$	$(x, y), (R_x, R_y)$	$(yz, xz)$

$C_5$	E	$C_5$	$C_5^2$	$C_5^3$	$C_5^4$	$\varepsilon = \exp(2\pi i/5)$	
A	1	1	1	1	1	$z, R_z$	$x^2 + y^2, z^2$
$E_1$	$\begin{Bmatrix} 1 & \varepsilon \\ 1 & \varepsilon^* \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon & \varepsilon^2 \\ \varepsilon^2 & \varepsilon^* \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^2 & \varepsilon^{2*} \\ \varepsilon^{2*} & \varepsilon^2 \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^{2*} & \varepsilon^* \\ \varepsilon^* & \varepsilon^2 \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^* & \varepsilon \\ \varepsilon & \varepsilon^* \end{Bmatrix}$	$(x, y), (R_x, R_y)$	$(yz, xz)$
$E_2$	$\begin{Bmatrix} 1 & \varepsilon^2 \\ 1 & \varepsilon^{2*} \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^2 & \varepsilon^* \\ \varepsilon^* & \varepsilon \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^* & \varepsilon \\ \varepsilon & \varepsilon^* \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon & \varepsilon^{2*} \\ \varepsilon^{2*} & \varepsilon \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^{2*} & \varepsilon^2 \\ \varepsilon^2 & \varepsilon^{2*} \end{Bmatrix}$		$(x^2 - y^2, xy)$

$C_6$	E	$C_6$	$C_3$	$C_2$	$C_3^2$	$C_6^5$	$\varepsilon = \exp(2\pi i/6)$	
A	1	1	1	1	1	1	$z, R_z$	$x^2 + y^2, z^2$
B	1	-1	1	-1	1	-1		
$E_1$	$\begin{Bmatrix} 1 & \varepsilon \\ 1 & \varepsilon^* \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon & \varepsilon^5 \\ \varepsilon^5 & \varepsilon \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^2 & \varepsilon^4 \\ \varepsilon^4 & \varepsilon^2 \end{Bmatrix}$	$\begin{Bmatrix} -1 & \varepsilon \\ \varepsilon & -1 \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon & \varepsilon^5 \\ \varepsilon^5 & \varepsilon \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^2 & \varepsilon^4 \\ \varepsilon^4 & \varepsilon^2 \end{Bmatrix}$	$(x, y), (R_x, R_y)$	$(yz, xz)$
$E_2$	$\begin{Bmatrix} 1 & \varepsilon^2 \\ 1 & \varepsilon^4 \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^2 & \varepsilon^4 \\ \varepsilon^4 & \varepsilon^2 \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^4 & \varepsilon^2 \\ \varepsilon^2 & \varepsilon^4 \end{Bmatrix}$	$\begin{Bmatrix} -1 & \varepsilon^3 \\ \varepsilon^3 & -1 \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^3 & \varepsilon^3 \\ \varepsilon^3 & \varepsilon^3 \end{Bmatrix}$	$\begin{Bmatrix} \varepsilon^3 & \varepsilon^3 \\ \varepsilon^3 & \varepsilon^3 \end{Bmatrix}$		$(x^2 - y^2, xy)$

58. State the rule that help determining the probability of a spectral transition.
59. Work out the irreducible representations of vibrational motion for (a) water, (b) ammonia, (c) methane, and (d) *trans*-N<sub>2</sub>F<sub>2</sub>.
60. State the essential criteria for a fundamental mode of vibration to be infrared and Raman active. Illustrate these with the fundamental modes of vibration in (a) water, (b) ammonia and (c) *trans*-N<sub>2</sub>F<sub>2</sub>.
61. Discuss the feasibility of electronic transitions in water, butadiene and benzene.
62. State the rule of mutual exclusion.
63. Determine the terms symbols for the d<sup>2</sup> configuration.
64. Explain how d orbitals split in energy in (a) an octahedral, and (b) tetrahedral environments.
65. (a) Work out the irreducible representations in (a) t<sub>2g</sub>, (b) e<sub>g</sub> and (c) e<sub>g</sub> configurations.  
 (b) Work out the splitting of the atomic terms of d<sup>2</sup> configuration in an octahedral environment.  
 (c) Draw qualitatively the correlation diagram of d<sup>2</sup> ion in an octahedral environment.
66. Explain the method of descending symmetry to ascertain the spin multiplicity of the states arising from the energy levels t<sub>2g</sub> and e<sub>g</sub> when the strong interactions of the ion with the octahedral environment is relaxed.
67. Draw qualitatively the correlation diagram of d<sup>2</sup> ion in a tetrahedral environment.
68. Work out the  $\pi$ -molecular orbitals and their energies for the molecule C<sub>4</sub>H<sub>4</sub>.  
 [Ans:  $\psi(A) = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_3)$ ;  $\psi(E_u) = \frac{1}{\sqrt{2}}(\varphi_2 - \varphi_4)$ ;  $E = \alpha$   
 $\psi(B) = \frac{1}{2}(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4)$ ;  $E = \alpha - 2\beta$   
 Work out the  $\pi$ -molecular orbitals and their energies of the molecule C<sub>8</sub>H<sub>8</sub>.  
 [Ans:  $\psi(A) = \frac{1}{\sqrt{8}}(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4 + \varphi_5 + \varphi_6 + \varphi_7 + \varphi_8)$ ;  $E = \alpha + 2\beta$   
 $\psi(B) = \frac{1}{\sqrt{8}}(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4 + \varphi_5 - \varphi_6 + \varphi_7 - \varphi_8)$ ;  $E = \alpha - 2\beta$   
 $\psi(E_{1a}) = \frac{1}{\sqrt{8}}(\sqrt{2}\varphi_1 + \varphi_2 - \varphi_4 - \sqrt{2}\varphi_5 - \varphi_6 + \varphi_8)$ ;  $E = \alpha + \sqrt{2}\beta$   
 $\psi(E_{1b}) = \frac{1}{\sqrt{8}}(\varphi_2 + \sqrt{2}\varphi_3 + \varphi_4 - \varphi_6 - \sqrt{2}\varphi_7 - \varphi_8)$ ;  $E = \alpha + \sqrt{2}\beta$   
 $\psi(E_{2a}) = \frac{1}{2}(\varphi_1 - \varphi_3 + \varphi_5 - \varphi_7)$ ;  $E = \alpha$   
 $\psi(E_{2b}) = \frac{1}{2}(\varphi_2 - \varphi_4 + \varphi_6 - \varphi_8)$ ;  $E = \alpha$   
 $\psi(E_{3a}) = \frac{1}{\sqrt{8}}(\sqrt{2}\varphi_1 - \varphi_2 + \varphi_4 - \sqrt{2}\varphi_5 + \varphi_6 - \varphi_8)$ ;  $E = \alpha - \sqrt{2}\beta$   
 $\psi(E_{3b}) = \frac{1}{\sqrt{8}}(\varphi_2 - \sqrt{2}\varphi_3 + \varphi_4 - \varphi_6 + \sqrt{2}\varphi_7 - \varphi_8)$ ;  $E = \alpha - \sqrt{2}\beta$ ]
70. Work out the irreducible representations for the vibrational modes of CO<sub>2</sub> and acetylene molecules. Also identify which ones of these are IR or/and Raman active.

The  $D_n$  Groups

	$E$	$C_n(z)$	$C_2(y)$	$C_2(x)$	
2	1	1	1	1	$x^2, y^2, z^2$
1	1	1	-1	-1	$xy$
1	1	-1	1	-1	$xz$
2	1	-1	-1	1	$yz$
3	1	-1	-1	1	$z, R_z$ $y, R_y$ $x, R_x$

	$E$	$2C_3$	$3C_2$	
3	1	1	1	$x^2 + y^2, z^2$
1	1	1	-1	$z, R_z$
2	1	-1	0	$(x^2 - y^2, xy), (xz, yz)$
2	-1	0	0	$(x, y), (R_x, R_y)$

	$E_2$	$2C_4$	$C_2(=C_4^2)$	$2C_2'$	$2C_2''$	
4	1	1	1	1	1	$(x^2 + y^2, z^2)$
1	1	1	1	-1	-1	$z, R_z$
1	1	-1	1	1	-1	$x^2 - y^2$
1	-1	1	1	-1	1	$xy$
2	1	-1	1	0	0	$(xz, yz)$
2	0	-2	0	0	0	$(x, y), (R_x, R_y)$

	$E$	$2C_6$	$2C_3$	$C_2$	$3C_2'$	$3C_2''$	
6	1	1	1	1	1	1	$x^2 + y^2, z^2$
1	1	1	1	1	-1	-1	$z, R_z$
1	1	-1	1	1	1	-1	$x^2 - y^2$
1	-1	1	1	1	-1	1	$xy$
2	1	-1	1	-1	0	0	$(xz, yz)$
2	1	-1	-1	1	0	0	$(x, y), (R_x, R_y)$
2	-1	-1	2	0	0	0	$(x^2 - y^2, xy)$

The  $C_{nv}$  Groups

	$E$	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$	
2	1	1	1	1	$z$
1	1	1	-1	-1	$R_z$
1	1	-1	1	-1	$x, R_x$
1	-1	1	-1	1	$y, R_y$
2	1	-1	-1	1	$xy, yz$

	$E$	$2C_3$	$3C_2$	
3	1	1	1	$x^2 + y^2, z^2$
1	1	1	-1	$z, R_z$
1	1	-1	0	$(x, y), (R_x, R_y)$
2	-1	0	0	$(x^2 - y^2, xy), (xz, yz)$

	$C_{nv}$	$E$	$2C_n$	$C_2$	$2\sigma_v$	$2\sigma_d$	
4	$A_1$	1	1	1	1	1	$x^2 + y^2, z^2$
1	$A_2$	1	1	1	-1	-1	$z, R_z$
1	$B_1$	1	-1	1	1	-1	$x^2 - y^2$
1	$B_2$	1	-1	1	-1	1	$xy$
2	$E$	2	0	-2	0	0	$(xz, yz)$

	$C_{6v}$	$E$	$2C_6$	$2C_3$	$C_2$	$3\sigma_v$	$3\sigma_d$	
6	$A_1$	1	1	1	1	1	1	$x^2 + y^2, z^2$
1	$A_2$	1	1	1	1	-1	-1	$z, R_z$
1	$B_1$	1	-1	1	1	1	-1	$x^2 - y^2$
1	$B_2$	1	-1	1	-1	-1	1	$xy$
2	$E_1$	2	1	-1	-2	0	0	$(xz, yz)$
2	$E_2$	2	-1	-1	2	0	0	$(x^2 - y^2, xy)$

4. The  $C_{nh}$  Group

	$C_{nh}$	$E$	$C_2$	$i$	$\sigma_h$	
2	$A_g$	1	1	1	1	$R_z$
1	$B_g$	1	-1	1	-1	$R_x, R_y$
1	$A_u$	1	1	-1	-1	$z$
1	$B_u$	1	-1	-1	1	$x, y$

	$C_{nh}$	$E$	$C_2$	$C_2^2$	$\sigma_h$	$S_2$	$S_4^2$	$S_4^4$	
4	$A'$	1	1	1	1	1	1	1	$x^2 + y^2, z^2$
1	$E'$	1	$\epsilon$	$\epsilon^*$	1	$\epsilon$	$\epsilon^*$	$\epsilon^*$	$(x, y)$
1	$A''$	1	$\epsilon$	$\epsilon$	1	$\epsilon^*$	$\epsilon$	$\epsilon$	$(x^2 - y^2, xy)$
1	$A''$	1	1	1	-1	-1	-1	-1	$z$
1	$E''$	1	$\epsilon$	$\epsilon^*$	-1	$-\epsilon$	$-\epsilon^*$	$-\epsilon^*$	$(R_x, R_y)$
1	$E''$	1	$\epsilon^*$	$\epsilon$	-1	$-\epsilon^*$	$-\epsilon$	$-\epsilon$	$(xz, yz)$

	$C_{nh}$	$E$	$C_4$	$C_2$	$C_4^3$	$i$	$S_4^2$	$\sigma_h$	$S_4$	
8	$A_g$	1	1	1	1	1	1	1	1	$R_z$
1	$B_g$	1	-1	1	-1	1	-1	1	-1	$x^2 + y^2, z^2$
1	$E_g$	1	$\epsilon$	$\epsilon^*$	$\epsilon$	1	$\epsilon$	$\epsilon^*$	$\epsilon^*$	$x^2 - y^2, xy$
1	$E_g$	1	$\epsilon$	$\epsilon$	$\epsilon^*$	1	$\epsilon^*$	$\epsilon$	$\epsilon$	$(R_x, R_y)$
1	$A_u$	1	1	1	1	-1	-1	-1	-1	$z$
1	$B_u$	1	-1	1	-1	-1	1	-1	1	$x^2 - y^2, xy$
1	$E_u$	1	$\epsilon$	$\epsilon^*$	$\epsilon$	-1	$-\epsilon$	$-\epsilon^*$	$-\epsilon^*$	$(xz, yz)$
1	$E_u$	1	$\epsilon$	$\epsilon$	$\epsilon^*$	-1	$-\epsilon^*$	$-\epsilon$	$-\epsilon$	$(x, y)$

	E	C <sub>6</sub>	C <sub>3</sub>	C <sub>2</sub>	C <sub>3</sub> '	C <sub>6</sub> '	i	S <sub>3</sub> <sup>S</sup>	σ <sub>H</sub>	S <sub>6</sub>	S <sub>3</sub>	R <sub>z</sub>	ε = exp(2πi/6)
A <sub>g</sub>	1	1	1	1	1	1	/	1	1	1	1	(x <sup>2</sup> +y <sup>2</sup> , z <sup>2</sup> )	
B <sub>g</sub>	1	-1	1	-1	1	-1	1	1	-1	1	-1		
E <sub>g</sub>	{ 1	ε	-ε*	-1	-ε	ε*	1	ε	-ε*	-ε	ε*	(R <sub>x</sub> , R <sub>y</sub> )	
	{ 1	ε*	-ε	-1	-ε*	ε	1	ε*	-ε	-ε*	ε	(xz, yz)	
T <sub>2g</sub>	{ 1	-ε	-ε*	1	-ε	-ε*	1	-ε	1	-ε	-ε*		(x <sup>2</sup> -y <sup>2</sup> , xy)
A <sub>u</sub>	1	1	1	1	1	1	-1	1	-1	-1	-1	z	
B <sub>u</sub>	1	-1	1	-1	1	-1	-1	1	1	-1	1		
E <sub>u</sub>	{ 1	ε	-ε*	-1	-ε	ε*	-1	ε*	ε	ε	-ε*	(x, y)	
	{ 1	ε*	-ε	-1	-ε*	ε	-1	ε	1	ε*	ε		
T <sub>1u</sub>	{ 1	-ε	-ε*	1	-ε	-ε*	-1	ε	-ε*	-ε	ε*		
E <sub>2u</sub>	{ 1	-ε	-ε*	1	-ε	-ε*	-1	ε	ε*	ε	ε*		

## The $D_{nh}$ Groups

$E$	$C_2(z)$	$C_2(y)$	$C_2(x)$	$i$	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$1_{2h}$	1	1	1	1	1	1	1
g	1	1	1	1	1	1	1
lg	1	-1	-1	1	1	-1	-1
2g	1	1	-1	1	-1	1	-1
3g	1	-1	1	1	-1	-1	1
u	1	1	1	-1	-1	1	-1
lu	1	-1	-1	-1	-1	1	1
2u	1	1	-1	-1	1	-1	1
3u	1	-1	1	-1	1	1	-1

## 6. The $D_{nd}$ Groups

$D_{2d}$	$E$	$2S_4$	$C_2$	$2C'_2$	$3\sigma_d$	$R_z$	$x^2 + y^2, z^2$ $x^2 - y^2$ $xy$ $(xz, yz)$
$A_1$	1	1	1	1	1		
$A_2$	1	1	1	-1	-1		
$B_1$	1	-1	1	1	-1		
$B_2$	1	-1	1	-1	1		
$E$	2	0	-2	0	0	$z$	

$D_{3d}$	$E$	$2C_3$	$3C_2$	$i$	$2S_6$	$3\sigma_d$	$R_z$	$x^2 + y^2, z^2$ $(x^2 - y^2, xy), (xz, yz)$
$A_{1g}$	1	1	1	1	1	1		
$A_{2g}$	1	1	-1	1	1	-1		
$E_g$	2	-1	0	2	-1	0		
$A_{1u}$	1	1	1	-1	-1	-1		
$A_{2u}$	1	1	-1	-1	-1	1		
$E_u$	2	-1	0	-2	1	0	$z$	

D <sub>4d</sub>	E	2S <sub>8</sub>	2C <sub>4</sub>	2S <sub>8</sub> <sup>3</sup>	C <sub>2</sub>	4C <sub>2</sub> '	4σ <sub>d</sub>	$x^2 + y^2, z^2$
A <sub>1</sub>	1	1	1	1	1	1	1	R <sub>z</sub>
A <sub>2</sub>	1	1	1	1	1	-1	-1	
B <sub>1</sub>	1	-1	1	-1	1	1	-1	
B <sub>2</sub>	1	-1	1	-1	1	-1	1	
E <sub>1</sub>	2	√2	0	-√2	-2	0	0	z
E <sub>2</sub>	2	0	-2	0	2	0	0	
E <sub>3</sub>	2	-√2	0	√2	-2	0	0	(x <sup>2</sup> -y <sup>2</sup> , xy)
								(R <sub>x</sub> , R <sub>y</sub> )
								(xz, yz)

The S<sub>2n</sub> Groups

S <sub>4</sub>	E	S <sub>4</sub>	C <sub>2</sub>	S <sub>4</sub> <sup>3</sup>	R <sub>z</sub>	(x <sup>2</sup> +y <sup>2</sup> , z <sup>2</sup> )
A	1	1	1	1		(x <sup>2</sup> -y <sup>2</sup> , xy)
3	1	-1	1	-1	z	
3	1	i	-1	-i	(x, y), (R <sub>x</sub> , R <sub>y</sub> )	(xz, yz)
	1	-i	-1	i		

S <sub>6</sub>	E	C <sub>3</sub>	C <sub>3</sub> <sup>2</sup>	i	S <sub>6</sub> <sup>5</sup>	S <sub>6</sub>	$\epsilon = \exp(2\pi i/3)$
A <sub>1</sub>	1	1	1	1	1	1	R <sub>z</sub>
A <sub>2</sub>	1	ε	ε*	1	ε	ε*	
E <sub>1</sub>	1	ε*	ε	1	ε*	ε	(R <sub>x</sub> , R <sub>y</sub> )
E <sub>2</sub>	1	1	1	-1	-1	-1	z
E <sub>3</sub>	1	ε	ε*	-1	-ε	-ε*	
E <sub>4</sub>	1	ε*	ε	-1	-ε*	-ε	(x, y)

## 8. The Cubic Groups

T	E	4C <sub>3</sub>	4C <sub>3</sub> <sup>2</sup>	3C <sub>2</sub>	$\epsilon = \exp(2\pi i/3)$
A	1	1	1	1	$x^2 + y^2 + z^2$
E	1	ε	ε*	1	
T	1	ε*	ε	1	(2z <sup>2</sup> -x <sup>2</sup> -y <sup>2</sup> , x <sup>2</sup> -y <sup>2</sup> )
	3	0	0	-1	(R <sub>x</sub> , R <sub>y</sub> , R <sub>z</sub> )
					(x, y, z)
					(xy, xz, yz)

T <sub>d</sub>	E	8C <sub>3</sub>	3C <sub>2</sub>	6S <sub>4</sub>	6σ <sub>d</sub>	$x^2 + y^2 + z^2$
A <sub>1</sub>	1	1	1	1	-1	$x^2 + y^2 + z^2$
A <sub>2</sub>	1	1	1	-1	-1	
E	2	-1	2	0	0	(2z <sup>2</sup> -x <sup>2</sup> -y <sup>2</sup> , x <sup>2</sup> -y <sup>2</sup> )
T <sub>1</sub>	3	0	-1	1	-1	(R <sub>x</sub> , R <sub>y</sub> , R <sub>z</sub> )
T <sub>2</sub>	3	0	-1	-1	1	(xy, xz, yz)

O	E	8C <sub>3</sub>	3C <sub>2</sub> (=C <sub>4</sub> <sup>2</sup> )	6C <sub>4</sub>	6C <sub>2</sub>	$x^2 + y^2 + z^2$
A <sub>1</sub>	1	1	1	1	1	$x^2 + y^2 + z^2$
A <sub>2</sub>	1	1	1	-1	-1	
E	2	-1	2	0	0	(2z <sup>2</sup> -x <sup>2</sup> -y <sup>2</sup> , x <sup>2</sup> -y <sup>2</sup> )
T <sub>1</sub>	3	0	-1	1	-1	(R <sub>x</sub> , R <sub>y</sub> , R <sub>z</sub> )
T <sub>2</sub>	3	0	-1	-1	1	(xy, xz, yz)

O <sub>h</sub>	E	8C <sub>3</sub>	6C <sub>2</sub>	6C <sub>4</sub>	3C <sub>2</sub> (=C <sub>4</sub> <sup>2</sup> )	i	6S <sub>4</sub>	8S <sub>6</sub>	3σ <sub>h</sub>	6σ <sub>d</sub>	$x^2 + y^2 + z^2$
A <sub>1g</sub>	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A <sub>2g</sub>	1	1	-1	-1	1	1	-1	1	1	-1	
E <sub>g</sub>	2	-1	0	0	2	2	0	-1	2	0	(2z <sup>2</sup> -x <sup>2</sup> -y <sup>2</sup> , x <sup>2</sup> -y <sup>2</sup> )
T <sub>1g</sub>	3	0	-1	1	-1	3	1	0	-1	-1	(R <sub>x</sub> , R <sub>y</sub> , R <sub>z</sub> )
T <sub>2g</sub>	3	0	1	-1	-1	3	-1	0	-1	1	
A <sub>1u</sub>	1	1	1	1	1	-1	-1	-1	-1	-1	(xz, yz, xy)
A <sub>2u</sub>	1	1	-1	-1	1	-1	1	-1	-1	1	
E <sub>u</sub>	2	-1	0	0	2	-2	0	1	-2	0	(x, y, z)
T <sub>1u</sub>	3	0	-1	1	-1	-3	-1	0	1	1	
T <sub>2u</sub>	3	0	1	-1	-1	-3	1	0	1	-1	

The Groups  $C_{\infty v}$  and  $D_{\infty h}$  for Linear Molecules

$C_{\infty v}$	$E$	$2C_{\infty}^{\phi}$	$\infty C_2$	$\infty \sigma_v$	$i$	$2S_{\infty}^{\phi}$	$\infty C_2$	
$A_1 \equiv \Sigma^+$	1	1	...	...	1	1	...	$z$
$A_2 \equiv \Sigma^-$	1	1	...	...	-1	1	...	$R_z$
$E_1 \equiv \Pi$	2	$2 \cos \phi$	...	...	0	$-2 \cos \phi$	...	$(x, y), (R_x, R_y)$
$E_2 \equiv \Delta$	2	$2 \cos 2\phi$	...	...	0	$2 \cos 2\phi$	...	$(xz, yz)$
$E_3 \equiv \Phi$	2	$2 \cos 3\phi$	...	...	0	$-2 \cos 3\phi$	...	$(x^2 - y^2, xy)$
...	...	...	...	...	...	...	...	...

$D_{\infty h}$	$E$	$2C_{\infty}^{\phi}$	$\infty C_2$	$\infty \sigma_v$	$i$	$2S_{\infty}^{\phi}$	$\infty C_2$	
$\Sigma_g^+$	1	1	...	1	1	1	...	$x^2 + y^2, z^2$
$\Sigma_g^-$	1	1	...	-1	1	1	...	$R_z$
$\Pi_g$	2	$2 \cos \phi$	...	0	$2 \cos \phi$	0	...	$(R_x, R_y)$
$\Delta_g$	2	$2 \cos 2\phi$	...	0	$2 \cos 2\phi$	0	...	$(xz, yz)$
...	...	...	...	...	...	...	...	$(x^2 - y^2, xy)$
$\Sigma_u^+$	1	1	...	1	-1	-1	...	$z$
$\Sigma_u^-$	1	1	...	-1	-1	-1	...	$(x, y)$
$\Pi_u$	2	$2 \cos \phi$	...	0	$-2 \cos \phi$	0	...	...
$\Delta_u$	2	$2 \cos 2\phi$	...	0	$-2 \cos 2\phi$	0	...	...
...	...	...	...	...	...	...	...	...

# APPENDIX I Units and Conversion Factors

## SI Units

There are seven base quantities in SI units. These are described in Table AI.1.

Table AI.1 Seven Basic Quantities in SI Units

Physical quantity	Name of unit	Symbol of unit	Definition
Length	meter	m	1650 763.73 wavelengths in vacuum of the radiation corresponding to the transition $2p_{10}-5d_5$ of the krypton-86
Mass	kilogram	kg	A cylinder of platinum-iridium alloy kept by the International Bureau of Weights and Measures in Paris
Time	second	s	The duration of 9 192 631 770 cycles of the radiation associated with the transition between the two hyperfine levels of the ground caesium-133 atom
Electric current	ampere	A	The magnitude of the current that, when flowing through each of two long parallel wires separated by one 1 m in free space, results in a force between the two wires of $2 \times 10^{-7}$ N for each meter of length.
Thermodynamic temperature	kelvin	K	Origin is at absolute zero and the triple point of water is 273.16 K
Amount of substance	mole	mol	Amount of substance that contains as many elementary entities (atoms, molecules, ions, etc.) as there are carbon atoms in 0.012 kg of carbon-12
Luminous	candela	cd	The luminous intensity, in the perpendicular direction, of a surface of 1/600 000 sq m of a black body at the temperature of freezing platinum under a pressure of 101.325 kPa

## Units Derived from the Base SI Units

Physical quantity	Name of unit	Symbol and definition
Force	newton	$N = \text{kg m s}^{-2}$ or $\text{J m}^{-1}$
Energy	joule	$J = \text{kg m}^2 \text{s}^{-2}$ or $\text{N m}$
Electric charge	coulomb	$C = \text{A s}$
Potential difference	volt	$V = \text{kg m}^2 \text{s}^{-3} \text{A}^{-1}$ or $\text{J A}^{-1} \text{s}^{-1}$
Resistance	ohm	$\Omega = \text{kg m}^2 \text{s}^{-3} \text{A}^{-2}$ or $\text{V A}^{-1}$
Frequency	hertz = cycle per second	$\text{Hz} = \text{s}^{-1}$
Area	square metre	$\text{m}^2$
Volume		cubic metre $\text{m}^3$
Density		kilogram per cubic metre $\text{kg m}^{-3}$
Velocity	metre per second	$\text{m s}^{-1}$
Angular velocity	radian per second	$\text{rad s}^{-1}$
Acceleration	metre per square second	$\text{m s}^{-2}$
Pressure	newton per square metre or pascal	$\text{N m}^{-2}$ or $\text{Pa}$
Conductivity	siemen	$S = \Omega^{-1}$
Magnetic fluid density	tesla	$T = \text{Wb m}^{-2} = \text{V s m}^{-2}$
Electric capacitance	farad	$F = \text{C V}^{-1}$
Magnetic flux	weber	$\text{Wb} = \text{V s}$
Inductance	henry	$H = \text{Wb A}^{-1}$

## CGS Units vis-à-vis SI Units

Physical quantity	CGS units		SI units	
	Name	Symbol	Name	Symbol
Length	centimetre	cm	metre	m
	Angstrom ( $10^{-8}$ cm)	Å		
Mass	gram	g	kilogram	kg
Time	second	sec	second	s
Temperature	{ celsius kelvin	{ °C °K	kelvin	K
Energy	calorie kilocalorie litre-atmosphere	cal kcal lit-atm	joule kilojoule	J kJ
Electric current	ergs ampere	erg A	erg ampere	A

## Conversion of CGS Units to SI Units

Quantity	Units	Equivalent <sup>†</sup>
Length	Angstrom, Å micron, μ	$10^{-10} \text{ m} = 10^{-1} \text{ nm} = 10^2 \text{ pm}$ $10^{-6} \text{ m}$
Volume	litre	$10^{-3} \text{ m}^3 = \text{dm}^3$
Force	dyne	$10^{-5} \text{ N}$
Energy	erg cal eV eV/mole	$10^{-7} \text{ J}$ 4.184 J $1.602 \times 10^{-19} \text{ J}$ 98.484 kJ mol <sup>-1</sup>
Pressure	atmosphere mmHg (or Torr) bar ( $10^6 \text{ dyn/cm}^2$ )	$101.325 \text{ kN m}^{-2}$ $133.322 \text{ N m}^{-2}$ $10^5 \text{ N m}^{-2}$
Viscosity	poise	$10^{-1} \text{ kg m}^{-1} \text{s}^{-1}$
Magnetic flux density (magnetic induction)	gauss	$10^{-4} \text{ T}$

<sup>†</sup> Symbols used for fractions and multiples are given in the next Table.

## SI Prefixes

Fraction	Prefix	Symbol	Multiples	Prefix	Symbol
$10^{-1}$	deci	d	10	deca	da
$10^{-2}$	centi	c	$10^2$	hecto	h
$10^{-3}$	milli	m	$10^3$	kilo	k
$10^{-6}$	micro	μ	$10^6$	mega	M
$10^{-9}$	nano	n	$10^9$	giga	G
$10^{-12}$	pico	p	$10^{12}$	tera	T
$10^{-15}$	femto	f	$10^{15}$	peta	P



Values of Some Physico-Chemical Constants

Constant	CGS units	SI units
Acceleration of gravity, $g$	980.66 cm sec <sup>-2</sup>	9.806 65 m s <sup>-2</sup>
Avogadro's constant, $N_A$	$6.022\ 05 \times 10^{23}$ molecules mole <sup>-1</sup>	$6.022\ 05 \times 10^{23}$ mol <sup>-1</sup>
Bohr magneton, $\mu_B$	$9.2741 \times 10^{-21}$ erg gauss <sup>-1</sup>	$9.27408 \times 10^{-24}$ A m <sup>2</sup>
Bohr radius, $a_0$	0.529 177 Å	$5.291\ 77 \times 10^{-11}$ m
Boltzmann constant, $k$	$1.380\ 66 \times 10^{-16}$ erg (degree K) <sup>-1</sup>	$1.380\ 60 \times 10^{-22}$ J K <sup>-1</sup>
Debye	molecule <sup>-1</sup>	
	$10^{-18}$ esu · cm	$3.335\ 6 \times 10^{-30}$ C m
Elementary charge, $e$	$4.802\ 98 \times 10^{-10}$ esu	$1.602\ 16 \times 10^{-19}$ C
Electronic rest mass, $m_e$	$9.109\ 53 \times 10^{-28}$ g	$9.109\ 53 \times 10^{-31}$ kg
Faraday constant, $F$	96 487 coulomb equiv <sup>-1</sup>	$9.648\ 46 \times 10^4$ C mol <sup>-1</sup>
	$8.31441 \times 10^7$ ergs (degree K) <sup>-1</sup> mole <sup>-1</sup>	$8.314\ 41$ J K <sup>-1</sup> mol <sup>-1</sup>
	$8.31441$ Joules (degree K) <sup>-1</sup> mole <sup>-1</sup>	$8.314\ 41$ N m K <sup>-1</sup> mol <sup>-1</sup>
Gas constant, $R$	$0.082\ 054$ litre-atm (degree K) <sup>-1</sup> mole <sup>-1</sup>	$8.314\ 41$ Pa m <sup>3</sup> K <sup>-1</sup> mol <sup>-1</sup>
	$1.987$ cal (degree K) <sup>-1</sup> mole <sup>-1</sup>	$8.314\ 41$ MPa cm <sup>3</sup> K <sup>-1</sup> mol <sup>-1</sup>

Molar volume of ideal gas

at 0°C and 1 atm,  $V_m$

22.414 litres

Permittivity of vacuum,  $\epsilon_0 = \mu_0^{-1} c^{-2}$

Permeability of vacuum,  $\mu_0$

Planck's constant,  $h$

Proton rest mass,  $m_p$

Vacuum speed of light,  $c$

Standard atmospheric pressure

76 cmHg

760 mmHg (or Torr)

1.0132 × 10<sup>5</sup> dynes/cm<sup>2</sup>

101.325 kPa

1.0132 5 bar

### Valence-Orbital Ionization Energies

Atom	$E_{1s}/\text{MJ mol}^{-1}$	$E_{2s}/\text{MJ mol}^{-1}$	$E_{2p}/\text{MJ mol}^{-1}$
H	1.317		
He	2.371		
Li		0.527	
Be		0.898	
B		1.353	0.802
C		1.880	1.030
N		2.466	1.269
O		3.125	1.533
F		4.478	1.808
Ne		4.681	2.083

## APPENDIX II Some Mathematical Expressions and Greek Alphabets

$$\sin \alpha \sin \beta = \frac{1}{2} \cos (\alpha - \beta) - \frac{1}{2} \cos (\alpha + \beta)$$

$$\cos \alpha \cos \beta = \frac{1}{2} \sin (\alpha - \beta) + \frac{1}{2} \sin (\alpha + \beta)$$

$$\sin \alpha \cos \beta = \frac{1}{2} \sin (\alpha + \beta) + \frac{1}{2} \sin (\alpha - \beta)$$

$$\sin (\alpha \pm \beta) = \sin \alpha \cos \beta \pm \cos \alpha \sin \beta$$

$$\cos (\alpha \pm \beta) = \cos \alpha \cos \beta \mp \sin \alpha \sin \beta$$

$$e^{\pm i\theta} = \cos \theta \pm i \sin \theta$$

$$\cos \theta = \frac{e^{i\theta} + e^{-i\theta}}{2}$$

$$\sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots$$

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \dots$$

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \dots$$

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \dots; \quad x^2 < 1$$

$$(1 \pm x)^n = 1 \pm nx \pm \frac{n(n-1)}{2!} x^2 + \frac{n(n-1)(n-2)}{3!} x^3 + \dots; \quad x^2 < 1$$

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}; \quad (n \text{ positive integer})$$

$$\int_0^\infty e^{-ax^2} dx = \left( \frac{\pi}{4a} \right)^{1/2}$$

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \dots (2n-1)}{2^{n+1} a^n} \left( \frac{\pi}{a} \right)^{1/2}; \quad (n \text{ positive integer})$$

$$\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}; \quad (n \text{ positive integer})$$

$$\int_0^a \sin \frac{n\pi x}{a} \sin \frac{m\pi x}{a} dx = \int_0^a \cos \frac{n\pi x}{a} \cos \frac{m\pi x}{a} dx = \frac{a}{2} \delta_{nm}$$

$$\int_0^a \cos \frac{n\pi x}{a} \sin \frac{m\pi x}{a} dx = 0; \quad (m \text{ and } n \text{ integers})$$

$$\int u v dx = u \int v dx - \int \left( \frac{du}{dx} \right) \int (v dx) dx$$

## Greek Alphabets

Symbol			Symbol		
Name	Roman	Italic	Name	Roman	Italic
Alpha	A	<i>A</i>	Nu	N	<i>N</i>
Beta	B	<i>B</i>	Xi	Ξ	<i>Ξ</i>
Gamma	Γ	<i>Γ</i>	Omicron	Ο	<i>ο</i>
Delta	Δ	<i>Δ</i>	Pi	Π	<i>Π</i>
Epsilon	Ε	<i>Ε</i>	Rho	Ρ	<i>ρ</i>
Zeta	Ζ	<i>Ζ</i>	Sigma	Σ	<i>σ</i>
Eta	Η	<i>Η</i>	Tau	Τ	<i>τ</i>
Theta	Θ	<i>Θ</i>	Upsilon	Υ	<i>υ</i>
Iota	Ι	<i>Ι</i>	Phi	Φ	<i>φ</i>
Kappa	Κ	<i>Κ</i>	Chi	Χ	<i>χ</i>
Lambda	Λ	<i>Λ</i>	Psi	Ψ	<i>ψ</i>
Mu	Μ	<i>Μ</i>	Omega	Ω	<i>ω</i>

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